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ANOMALOUS ATOMIC WEIGHTS IN THE D. I. MENDELEEV PERIODIC SYSTEM

G. P. Maltak

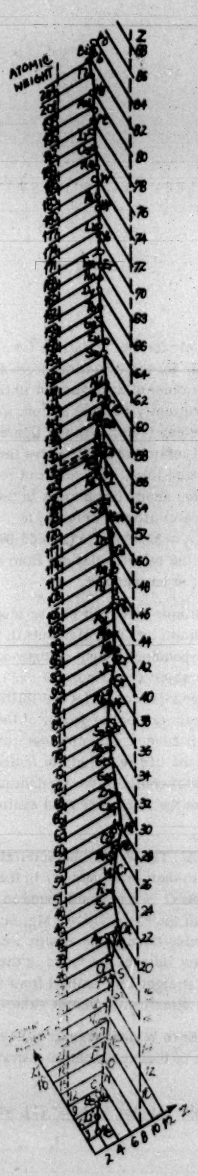
The consolidation zones in the atomic system [1] are the reason, not only for the deviations from the general rules that hold for the properties of the atoms contained in it, but also for the deviations from a uniform increase in the atomic weights of the elements as a function of their order of arrangement in the periodic system of D. I. Mendeleev. The relationship existing between the currently adopted atomic weights of the elements and their order number in the periodic system of D. I. Mendeleev is shown in the figure proposed here, where in order to reduce the area of the empty fields and still retain the whole curve the designations of the rectangular coordinates are extended along the broken dotted lines. The zones of relative consolidation in the atomic system are the reason, not only for the three known anomalies present in the D. I. Mendeleev periodic system, consisting in that the elements with the greater atomic weights are arranged before those with lower atomic weights: Ar (A = 39.944) before K (A = 39.096), Co (A = 58.94) before Ni (A = 58.69) and Te (A = 127.61) before I (A = 126.92), but also for the other deviations from a uniform increase in the atomic weights of the elements with increase in their order numbers.

When these deviations are compared with the rules prevailing for the atomic system it can be seen, at either the top or bottom of the figure, that atomic weight deviations are shown by those elements in whose series in the table the consolidation zones pass through either heavy or, correspondingly, light isotopes and cause an abnormally high diffusion and stability of those atoms, which in the absence of a zone of consolidation would be radioactive, and in this way showing deviation from the general course for the shifting of the group numbers of the predominant isotopes of these elements to the larger or smaller groups of the system. This occurs most frequently in the right zone of the table. In the left zone, containing less stable atoms, the described consolidation zones for the most part only cause an increase in the life period of the radioactive elements through which they pass. Arising as a result of this, the unsymmetrical course of the predominant isotopes of the pleiads in the right and left zones of the table is responsible for the three indicated anomalies present in the periodic system of D. I. Mendeleev.

We will examine two portions of the curve in the figure: C, N, O and Hf, Ta, W, Re, characterizing the most uniform change in the atomic weights of the elements with change in their order number in the periodic system of D. I. Mendeleev. The predominant isotopes of the elements C, N and O are found in like zero groups of the atomic system, the same as the predominant isotopes of the elements Ne, Mg, Si and S, the atomic weights of which also fall quite well in the figure on a line passing through the atomic weights of the elements C, N and O. For the elements F, Na, Al and P the predominant isotopes are found in the first group, based on the larger group unit, and their atomic weights fall on a straight line, shifted from the line, passing through the atomic weights of C, N, O, Ne, Mg, Si and S, in the direction of greater values.

The group* numbers of the more diffuse isotopes of the elements from Er to W show regular increase with increase in the element order number; for this reason the atomic weights of these elements are arranged

* Here and later the references to groups and series are to be found in the table "Atomic System" [1], which for brevity is also called simply "table" or "system".



correctly in the direction of the curve shown in the figure, and here it is steeper than for the portion from C to S. From the figure, on a larger scale, it can also be seen that the atomic weights of the elements with odd Z are arranged on this portion of the curve somewhat below the atomic weights of the elements with even Z. The following is responsible for this. On this portion the arithmetic mean of the group numbers of the two most diffuse isotopes of each given element with even Z is greater by 2 than the group number of the predominant isotope of the preceding element with odd Z and equal to the group number of the predominant isotope of the following element with odd Z. Thus, the two most diffuse isotopes [2] of Er, constituting 33 and 27% of the pleiad, are respectively found in the 30th and 32nd (arithmetic mean 31) groups of the system. For the following element Tm the predominant isotope, constituting 100% of the pleiad, is found in the 31st group of the system. For Yb, the next element, with even Z, the two most diffuse isotopes, representing 32 and 22% of the pleiad, are respectively found in the 34th and 32nd (arithmetic mean 33) groups. The predominant isotope of Lu, constituting 97% of the pleiad, is found in the 33rd group. The two most diffuse isotopes of Hf, constituting 35 and 27% of the pleiad, are respectively found in the 36th and 34th (arithmetic mean 35) groups of the system. The predominant isotope of Ta, constituting 100% of the pleiad, is found in the 35th group. For W, the next element, with even Z, the two most diffuse isotopes, constituting 31 and 29% of the pleiad, are respectively found in the 36th and 38th (arithmetic mean 37) groups of the system.

We will now examine the greatest deviations from a uniform change in the atomic weights of the elements with change in their order numbers. From the figure it can be seen that they consist in the abnormally high atomic weight of the element Ba and in the already mentioned three anomalies: Te – I, Co – Ni, Ar – K.

The abnormally high atomic weights for the elements Ba and Te, deviating, as can be seen from the figure, from the uniform course of change in the atomic weights of the elements with change in their order numbers, are determined by the fact that a zone of consolidation passes through their heaviest stable isotopes, as a result of which they predominate in pleiads. The predominant isotope of Ba is its heaviest isotope Ba^{138}_{56}, constituting 72% of the pleiad and predominating in the 26th group, while second in diffusion is its second heavy isotope Ba^{137}_{56}, constituting 11% of the pleiad, which in the absence here of a consolidation zone would be β^--radioactive. The predominant tellurium isotope Te^{130}_{52} and itself the only heavy isotope of those met with in the family of isotopes for this element, constituting [2] 34% of the pleiad, in the absence of this consolidation zone would also be β^--radioactive. The group numbers in the table "System of Atoms" of the

predominant isotopes of Ba and Te deviate from the general direction of the change in the group numbers of the predominant isotopes of the pleiad with change in Z. In the transition from Ru to Sn they are shifted uniformly to the right. The predominant isotope of Ru is found in the 14th group, of Pd in the 14th and 16th, of Cd in the 16th and 18th, and that of Sn in the 18th. But in the transition to Te it is shifted sharply to the right, into the 26th group of the table, through which in this series a consolidation zone passes. For Ba it is also found in the 26th group, but already on the diagonal portion of the consolidation zone, and then it turns to the left, being situated in the following Ce and Nd series exactly on a line with the diagonal portion of the zone, correspondingly found in the 24th and 22nd groups, after which it emerges from the consolidation zone and in the following series it is again uniformly shifted to the right. As a result, the deviation of the atomic weights for Te and Ba is due to the rules that have been laid down for the atomic system. On the basis of these rules it can be assumed that for Xe also the predominant isotopes are actually located closer to the diagonal portion of the consolidation zone than is indicated in the table "System of Atoms" and from the contemporary data for the composition of this pleiad [2], and that the atomic weight of cosmic Xe is greater than the values currently adopted for it. In the Kr series, where the situation in many respects is comparable, this fails to exist. The predominant isotope of Kr fails to separate from the predominant isotopes of Se and Sr, as does the predominant isotope of Xe from the predominant isotopes of Te and Ba, but instead is found with them in one group in the table. In accord with this on the curve in the figure Kr is found at the apex of the salience, conditioned by the consolidation zone. If in actuality the consolidation zone also shifts the predominant isotopes of cosmic Xe in the same manner and on the curve in the figure, it (Xe) is also found at the apex of the salience, conditioned by the consolidation zone, then, as can be seen from the dotted line construction on this figure, its atomic weight can be close to or even exceed the atomic weight of Cs.

The consolidation zone, conditioning (determining) in the system the sharp displacement to the right of the predominant isotopes of Te and Ba, and in the La series toward the left zone in the table, is responsible for the stability of the isotopes La_{57}^{138} and La_{57}^{139}, which in the absence of this zone would be β^--radioactive, and consequently the atomic weight of lanthanum is also shifted slightly upward on the curve in the figure. In the Cs, I and Sb series this zone traverses the regions that are more remote from the central isotopes of the pleiad and the more short-lived β^--radioactive atoms and appears only when their life period is increased, failing to exert an influence on the atomic weights of these elements. Consequently, in the series found in the left-hand zone of the table from Rh to La the group numbers of the predominant isotopes of the pleiads change uniformly: Rh in the 13th group, Ag in the 15th, In in the 17th, Sb in the 19th, I in the 21st, Cs in the 23rd, and La in the 25th. In like manner, the atomic weight of I also fails to deviate from the line connecting the atomic weights of these elements, which line is shown in the figure as a dotted line. As a result, the anomalous change in atomic weight on going from Te to I is determined by the deviation in the atomic weight of Te toward larger values, which deviation is due to the fact that of the isotopes, encountered in its type, the heaviest are found in the atomic system in the consolidation zone and consequently they predominate in the pleiad.

In contrast to the anomalous change in atomic weight shown in the transition from Co to Ni, the change shown for Ni can be explained. In its position the predominant isotope of Co fails to be separated from the predominant isotopes of its neighboring series in the table. The predominant isotopes of V, Mn, Co and Cu are found in a single group, the 5th group in the left-hand zone of the table. In accord with this the atomic weight of Co also fails to deviate from the general course of change in the atomic weights of the elements with change in the order numbers and is found on the straight line, passing through the atomic weights of V, Mn and Cu, and designated in the figure by a dotted line. On the other hand, in the table the position of the predominant isotope of Ni deviates from the general course of change in the group numbers of the predominant isotopes of the elements with change in their order numbers. In three series of the system, preceding the Ni series, in the Ti, Cr and Fe series and in the following Zn series the predominant isotopes are found in one group, the 4th group of the system, while the predominant Ni isotope is found in the 2nd group. This deviation in the group number of the predominant Ni isotope in the direction of lighter atoms determines the abnormally low atomic weight shown by this element, deviating from the general course of change in the atomic weights of the elements with change in their order numbers. This abnormal behavior is conditioned by the fact that for Ni the lightest isotope encountered in its family of isotopes, namely Ni_{28}^{58}, is found in the system on the diagonal portion of the consolidation zone and for this reason it predominates in the pleiad.

We will now examine the anomaly in the change of the atomic weight values in the transition from Ar to K. The predominant isotope of potassium and the predominant isotopes of the five series preceding it in the system: F, Na, Al, P and Cl, are all found in a single group, the 1st group of the system; consequently, the atomic weight of K is also found on a straight line, connecting the atomic weights of these elements and designated in the figure by a dotted line. However, the position of the predominant isotope of K already deviates somewhat from the general course of change in the group numbers of the predominant isotopes of the pleiad along the rows of the zone of uneven Z numbers, and the curve for the change in the weights of the elements as a function of their order numbers, not being a straight line, under a uniform course should have shown in the figure a steeper passage here than for the dotted line and somewhat above the actual position of K. This is conditioned (determined) by the still not investigated consolidation zone, which appears here and in the deviations of the half-life period of the radioactive atoms of the zero and 2nd groups, situated adjacent to K^{39}_{19}. However, the deviation in the atomic weight of K from the values, corresponding to a uniform course of change in the atomic weights of the elements with change in their order numbers in the direction of lower values, is nevertheless slight, and in itself cannot cause the examined anomaly. Responsible for it in much greater measure is the deviation of the atomic weight of Ar from the general course of change in the atomic weights of the elements with change in their order numbers in the direction of greater values. The position of Ar^{40}_{18}, the predominant isotope of argon, according to contemporary data [2] constituting 99,632 % of the pleiad, deviates sharply from the general course shown by the group numbers of the predominant isotopes of the neighboring series. In the six series in the table preceding the Ar series, the C, O, Ne, Mg, Si and S series, and in the Ca series following it, the predominant isotopes are found in the zero group, while the predominant isotope of Ar is found in the 4th group. This sharp deviation shown by the group number of the predominant Ar isotope in the direction of the heavier atoms explains the abnormally greater atomic weight of Ar. However, in the rules for the change in the properties of the atoms, in the table found adjacent to the predominant argon isotope Ar^{40}_{18}, there fail to be other anomalies that would be in agreement with such a sharp deviation in the group number of the predominant Ar isotope. The curve for the diffusion of the atoms in the 4th group descends from a maximum, corresponding to the atom Fe^{56}_{26}, at first in the direction of the light atoms, in the transition to Cr^{52}_{24}, sharply, and then in the transition from Ti^{48}_{22} to Ca^{44}_{20} very insignificantly, so that for the atom Ar^{40}_{18}, the cosmic diffusion of which had not been determined [3], there can be and does correspond a second maximum on the diffusion curve for the atoms of this group, after which it descends more sharply for the S^{36}_{16} atom. However, taking into consideration the diffusion values given in the table for the S^{36}_{16} and Ca^{44}_{20} atoms and noting, in general, the higher diffusion in most of the groups of the atoms, adjacent to the predominant isotopes, when compared with the diffusion of the atoms further removed from it, and also the absence of any kinds of deviations in the course of change for the properties of the adjacent β^--radioactive atoms of the 5th group, it is impossible to expect a greater value for the relative cosmic diffusion of the Ar^{40}_{18} atom.

Since the diffusion relationship of the atoms in the cosmos should to a large degree correspond to the relationship established for them as a function of their stability in the process of natural development and for that reason be in better agreement with the rules for the change in the other properties of the atoms in the system, whereas the other anomalies in this region of the system fail to correspond to the indicated sharp displacement of the group number of the predominant isotope, according to contemporary data [2], found in the composition of the Ar pleiad, then, probably, as has already been repeatedly mentioned, the atom Ar^{40}_{18} is not the predominant isotope in the composition of cosmic Ar. In any case it can be assumed that the amount of atom Ar^{40}_{18} in cosmic Ar is less than the amount that has been used up to now for Ar, and consequently the atomic weight of Ar will be less than the value assumed for it now, for which reason an anomalous atomic weight change in the transition from Ar to K fails to exist.

However, it is necessary to mention that at the present time the properties of the heavier (heavier than those indicated in the table) isotopes of Ar, S and their neighboring series are still not known. However, the consolidation zone, the diagonal portion of which, in the direction from Ni^{57}_{28} to Ca^{44}_{20}, passes through the atoms with $Z + N \approx 28$, apparently embraces the atoms in these series also; consequently, a greater longevity and even stability can be assumed for the Ar isotope with an even mass number greater than 40. The fact that it has not been revealed up to now gives basis to assume that it is not widely diffused and consequently it cannot exert a great influence on the atomic weight of Ar. However, the fact that the consolidation zone does embrace the heavy isotopes of Ar, by analogy with the situation that prevails in the Kr and Xe series, gives some basis for the displacement of the group number of the predominant Ar isotope. The

displacement to the right of the predominant isotopes of Kr and Xe, determined by the consolidation zones, which are also responsible for the stability of the atoms Kr^{86}_{36}, Xe^{134}_{54} and Xe^{136}_{54}, through which they pass in these series, would also be less valid if in these and their adjacent series, the same as in the Ar series and those adjacent to it, the properties of the atoms, arranged in the table to the right of Kr^{86}_{36} and Xe^{133}_{54}, in this direction found directly after the predominant isotopes of these pleiads, were unknown, and if not the zones were examined, but only the atoms, situated close to the predominant isotopes of these pleiads.

However, even with an appraisal of this nature the displacement of the predominant Kr and Xe isotopes agrees better with the other data than does the displacement of the predominant Ar isotope. The position in the table of the predominant Ar, Kr and Xe isotopes with respect to the predominant atoms of their groups, found in the consolidation zones, is variable. Ar^{40}_{18} is removed from Fe^{56}_{26}, the predominant atom of the 4th group, Kr^{84}_{36} and the predominant atom of the 12th group, Sr^{88}_{38}, are found in adjacent rows, Xe^{132}_{54} is situated one row away from Sn^{124}_{50} and Ce^{140}_{58}, the predominant atoms of the 24th group, and it can be assumed that actually the predominant Xe isotope is displaced even more to the right, and consequently, as can be seen from the table, is found even closer to the predominant atom of its group and to the consolidation zone. In addition, the predominant isotopes are displaced sharply to the right also in several of the series preceding Kr and Xe, while in the series following directly after them they are displaced not to the right, which is in accord with the general rules, but to the left, being situated along the diagonal portion of the consolidation zone. In the series directly following Ar, the predominant isotopes show such displacement in the consolidation zone only for Cr, Fe and Ni. The predominant isotope of Ti only adjoins it, while calcium is completely removed. If the predominant isotope of cosmic Ar, its most stable isotope, is actually displaced toward the consolidation zone, then the predominant isotope of Ca should also be displaced toward the heavy stable isotope, found in the same consolidation zone, and the greater diffusion value, indicated at the present time [2] for Ca^{40}_{20}, can then be assumed to be conditioned by secondary processes. According to contemporary data, the Ca^{48}_{40} atom, which in the absence of a consolidation zone would be β^--radioactive, shows slight diffusion, but more than does Ca^{46}_{20}, which is found closer to the center of the pleiad. For conclusive evidence relative to the Ar—K anomaly and for answering the questions raised here in connection with it it will require making further experimental studies.

As a result, the deviations from a uniform change and the anomalous atomic weights found in the D. I. Mendeleev periodic system are conditioned by a fundamental property of the atomic system — by the consolidation zones, characterizing the periodicity in the atomic system, which periodicity is associated with the periodicity in the D. I. Mendeleev system of the elements. This corresponds to the statements of D. I. Mendeleev on the fundamental significance of atomic weights in the periodic system of the elements. Using this as a basis, he established and corrected the atomic weights and, not having at that time a basis to suspect the peculiarity of the examined anomalies, deemed it probable that they also were due to inaccurate atomic weight determinations. After the discovery of the second basic characteristic of an atom — the nuclear charge, coinciding with the order (atomic) number of the element in the D. I. Mendeleev system, and the confirmation of the named anomalies by means of new atomic weight measurements, the significance of atomic weights in the periodic system of the elements began to be considered as reduced in importance. However, these anomalies and the deviations, bringing out the connection between the periodic system of the elements and the atomic system, only confirm the fundamental significance of atomic weights.

SUMMARY

When the known anomalies and other atomic weight deviations of the elements in the D. I. Mendeleev periodic system are compared with the rules laid down for the atomic system, it can be seen that those elements show atomic weight deviations in whose series in the table "System of Atoms" the consolidation zones pass through either heavy or light isotopes, causing their abnormally high diffusion (distribution) and the stability of those atoms, which in the absence of a consolidation zone would be radioactive. This occurs most frequently in the right-hand zone of the table. In the left-hand zone, having less stable atoms, the earlier described consolidation zones in the majority of cases show up only as an increase in the life span of the radioactive atoms through which they pass. The lack of symmetry arising as a result of this in the right-hand and left-hand zones of the table "System of Atoms" is the reason for the indicated anomalies and atomic weight deviations shown by the elements in the periodic system of D. I. Mendeleev.

As a result, the examined anomalies and atomic weight deviations reflect in the D. I. Mendeleev periodic system a fundamental property of the atomic system – the consolidation zones, which characterize the periodicity in the atomic system, in turn associated with the periodicity shown in the table of D. I. Mandeleev. Having shown the bond existing between the rules laid down for the periodic system of the elements and the rules formulated for the atomic system, these anomalies and deviations only confirm the fundamental significance possessed by atomic weights in the D. I. Mendeleev periodic system.

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* T.p. = C. B. Translation pagination.

THE APPLICATION OF THE V. F. ALEKSEEV RULE TO TERNARY SYSTEMS*

I. L. Krupatkin

In 1885 a rule was formulated for the mutual solubility diagrams of liquids composing binary two-phase liquid systems [1], widely known in the literature under the name of the Alekseev rule. The rule was defined as follows [2]: "The geometric location of the conode centers, drawn through the figurative points of two conjugated liquid phases, is nearly a straight line, provided the composition of the system is expressed in either weight fractions or percents".

The Alekseev rule permits determining the coordinates of the critical solution point on the equilibrium curve between the liquid phases of the system, for which reason it is widely used in studying two-component systems for layer-formation. On the one hand, the objective of the present work was to show that the Alekseev rule is also applicable to three-component systems, and on the other hand, that the line passing through the center of the conode (median line) possesses a definite physicochemical significance. As a result of this, the limits of use for the Alekseev rule are greatly extended, and the essence of its physicochemical significance is uncovered.

To study the indicated problems we will first examine such a ternary system as contains one binary system with layer-formation, capable of homogenization by a third component with respect to itself. In the simplest case, when in the binary systems of the given ternary system chemical compounds fail to be formed, the mutual solubility isotherm for the liquid phases will have the form (Fig. 1) of the binodal curve 1, K, 2. In similar cases the position of the conode in the two-layer region will not be fortuitous, but will be closely associated with the reactivity between the components in the component binary systems and in the ternary system as a whole. All three of the binary systems, composing the given ternary system, participate in the general reactivity found in the ternary system. However, among them there is always found such a binary system as shows stronger reactivity than do the other two binary systems, i. e. it predominates over the reactivity shown in the other binary systems. Such a binary system in the given type of ternary system was called [3] the predominant system. The latter is very easily found from the position of the conode in the two-layer region, and specifically conodes arranged in the shape of an open fan. As a result, for the ternary system A – B – C (Fig. 1) the binary system A – C is the predominant one. The point K of the binodal curve is the critical isothermal solution point [4].

In two-component systems with layer formation the conodes are parallel to each other and to the concentration axis, and the upper critical solution point appears as the maximum point on the binodal curve. The median line, passing through the center of the conode, descends into the critical point and will be almost a straight line. In this way it is possible to find the median line on the mutual solubility isotherms of the liquid phases in three-component systems. This line, beginning at point m, i. e. in the middle of the limiting conode 1, 2, of necessity ends in the critical isothermal solution point K. This circumstance is associated with the fact that in binary systems with limited solubility for the liquid

* The studies of N. A. Izmailov and A. K. Franke, J. Phys. Chem. 29, 120, 263, 620 (1955), appeared in this field, but in a somewhat different direction.

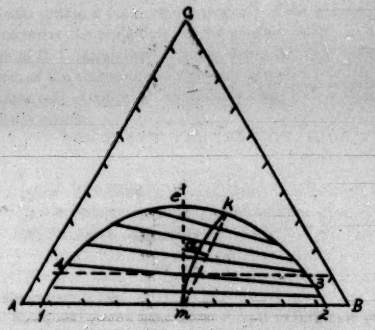

Fig. 1. Solubility isotherm of a ternary system with one binary layer formation.
Explanation in the text.

phases the interrelationships between the components are weakened, and that when a homogenizer C is added to the stratified components A and B the interrelationships between them are strengthened, and the mutual solubility of the liquid phases increases. As a result of this the conode length is reduced, and in the final end they are converted into the critical point K. However, in ternary systems the conodes are not parallel, either to each other or to the limiting conode 1, 2, the latter being adjacent at the same time to the binary stratified system A B. This is explained by the fact that when compared with the binary systems, in the ternary systems the relationships are complicated by the presence of a third component and the dissimilar interrelationships prevailing in the binary homogeneous systems that are formed by this third component (a matter that will be discussed in more detail below); consequently, it is necessary to elucidate on concrete examples of ternary systems the character and direction of the median line in them. It should be mentioned that in the literature there exist only a relatively small number of investigated ternary systems of the indicated type, in which a large number of conodes would be determined. Nevertheless, it is possible to make some definite conclusions relative to the investigated problem from the already existing literature data; in which connection it is possible to isolate two types of systems (although the possibility of other types also being present is not excluded) from this data. We will present some examples of these two types.

The solubility isotherm with conodes is presented for the ternary system water-ethyl ether-triethylamine [5] at 0° (Fig. 2). At this temperature the given system satisfies the examined type of equilibrium diagram. Beginning with 18° and higher there arises stratification in the binary system triethylamine-water from the lower critical temperature, and in the given ternary system an equilibrium region is realized between the liquid phases, connecting the solubility breaks found in the two binaries of its system. The critical isothermal solution point K is shifted toward the binary system triethylamine-water. The conodes are

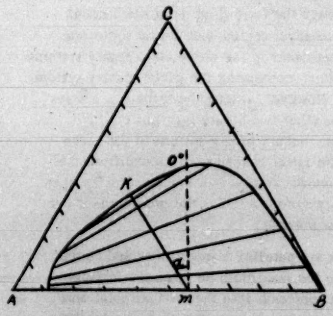

Fig. 2. Solubility isotherm of the ternary system water-ethyl ether-triethylamine at 0 deg.
A) water, B) ethyl ether, C) triethylamine.
Straight line Km--median line

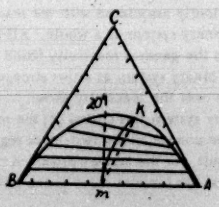

Fig. 3. Solubility isotherm of the ternary system water 1, 2-Dichloroethane-ε-caprolactam at 20 deg.
Curve Km) median line;
A) water, B) 1,2-dichloroethane
C) ε-caprolactam.

distributed as a spreading fan toward the binary system triethylamine-ethyl ether; consequently, this system will be predominant. The construction of the median line shows that it is a straight line, passing through the critical isothermal solution point K. If in the center of the limiting conode, i. e. at point m, a perpendicular is drawn toward the stratified binary system water-ethyl ether, then (Fig. 2) the median line deviates from this vertical by a definite angle α, in a direction away from the predominant binary system triethylamine ethyl ether. A similar case is found in the ternary system water-chloroform- ϵ-caprolactam [6]. In this system also the median line is a straight line, passing through the critical point and being slanted away from the predominant binary system ϵ-caprolactam-chloroform.

The ternary system water- 1, 2-dichloroethane- ϵ-caprolactam [6], with a somewhat different character for the median line, is shown in Fig. 3. For this ternary system the binodal curve with conodes is given at 20°. The conodes are distributed as a spreading fan toward the binary system 1, 2-dichloroethane- ϵ-caprolactam, which, consequently, appears as the predominant system. The critical isothermal solution point K, through which the median line passes, being slanted in a direction away from the predominant binary system 1, 2-dichloroethane- ϵ-caprolactam, is shifted toward the binary system water- ϵ-caprolactam. However, it is characteristic that in this case the median line is not a straight line; instead, it is a curve, being convex with respect to the predominant system. A similar situation is observed in the following ternary systems: water methylene chloride- ϵ-caprolactam [6], water-chloroform-acetic acid [7], water-ethyl alcohol-amyl alcohol [8], water-pyridine-benzoic acid [9], and water-isopropyl alcohol-isopropyl ether [10]. In them also the median lines are curves, being convex with respect to the predominant systems, but always being inclined away from them.

As a result, the described facts show that the Alekseev rule is not only applicable to binary, but also to three-component systems; in this connection the median line in the ternary system is in general a curve, although it can also be a straight line. This median line passes through the critical isothermal solution point, for which reason the Alekseev rule can be used in ternary systems for finding the coordinates of the indicated critical point. This question is especially important for the ternary systems since their binodal curves are very gently sloping, and even near the critical point the conodes possess considerable length; for this reason it is difficult to establish the exact composition, corresponding to the critical point, by them. But the application of the Alekseev rule to ternary systems is not limited to this; it can also be utilized for finding the predominant binary system. Actually, as the presented material shows, of the three component binary systems in a ternary system the predominant one will be that system where the median line is slanted away from it in relation to the perpendicular, drawn through its point of intersection with the side binary system showing stratification.

The direction of the median line not only bears a geometric character, but it also possesses its own physicochemical reasons. As was already indicated, the character of conode distribution on the mutual solubility isotherms of the liquid phases in a ternary system is determined by the interrelationships existing between the components of the system and peculiarly reflects these relationships. The conodes are directed by the spreading fan toward the predominant binary system. But the median line is closely associated with the conodes, it is derived from the data on the conodes and on the compositions of the coexisting liquid phases; for this reason the median line reflects the general character of conode distribution and that way in turn reflects the interrelationships that exist between the components of the ternary system. The presented factual material shows that the median line is slanted away from the perpendicular, drawn through the middle of the limiting conode, by a definite angle α in the direction away from the predominant binary system in the given ternary system. It should be mentioned here that since the interrelationships between the components can change with temperature change, then for the different isotherms in the same ternary system the direction and character of the median line can be dissimilar, i. e. they also can change. In this way the transition from an isothermal to a polythermal examination of the changes in the system can be made.

It is necessary to mention that the processes taking place in a ternary system, disregarding their character, were associated above with the direction and form of the median line. These processes are frequently associated with the distribution of the conodes in the stratification region [11]. These same processes can also be associated with the position of the critical points on the stratification isotherms. The deviation, observed in the vast majority of cases, shown by the critical isothermal solution point in a ternary system of the type of A–B–C (Fig. 1) from the maximum point on the binodal curve for a certain portion of its section can be considered as being due to dissimilar interrelationships existing between the components of the immiscible binary system A–B and the homogenizer C. If we assume

that these interrelationships are stronger with component A than they are with component B, then the binary system A–C will appear as the predominant one. When component C is added to the system A–B or to a heterogeneous mixture P, we in this way add the same amount (in percent) of C to both of the components A and B, but it will show a different distribution by phases. On the strength that the interrelationships between components A and C are stronger, and those between B and C weaker, then component C will distribute itself in such manner that in the phase with the greater content of A it will be present in greater amount, and in the phase with the greater content of B it will be present in lesser amount; consequently, in the composition triangle the first phase, corresponding to point 4, will be situated closer to the angle of component C while the second coexisting phase, corresponding to point 3, will be further removed from it. As a result of this, the conode 3, 4 (and all of the other conodes) will fail to be parallel to the side of the binary system A–B, and will deviate from the horizontals in the direction of the binary system B–C. Consequently, the critical point K will also be shifted in the direction of the same binary system. As a result, some understanding as to the relationships existing between the components of a ternary system can also be gained from the degree of shifting shown by the critical isothermal solution point with respect to the maximum on the binodal curve for a certain length of its section.

The indicated possibility of approaching a description of the relationships existing between the components of a ternary system from different sides is explained by the fact that all of these geometric elements–the conodes, median line, and critical point, together with the binodal curve–constitute a single whole. This whole complex is based on equilibrium existing between the liquid phases, and together with the surface of this equilibrium, reflects the physicochemical processes that proceed in the system. Consequently, these processes can be described from any of the above indicated viewpoints, but they would be most completely characterized by all of the mentioned geometric elements, taken together.

Above we described the application of the Alekseev rule to the simplest type of ternary systems with one immiscible binary system and without the formation of chemical compounds between the components. Nevertheless, this same rule can also be applied to more complex cases of liquid phase equilibria with two immiscible binary systems and with the formation of chemical compounds. The Alekseev rule is based on physicochemical considerations, which are clearly elucidated on the examples of ternary systems, but which can also be elucidated on the examples of binary systems. However, all of these questions require separate examination.

SUMMARY

1. It was shown on concrete examples that the Alekseev rule is fully applicable to ternary systems having equilibrium between the liquid phases.

2. It was shown that the median line on the equilibrium isotherm for the liquid phases in a ternary system is in general a curve (it can also be a straight line), beginning at the center of the limiting conode and ending in the critical isothermal solution point. In this way the Alekseev rule can be utilized for determining the coordinates of the indicated critical point.

3. It was shown that the Alekseev rule is based on physicochemical considerations. The character of the median line reflects the relationships existing between the components present in the ternary system. The median line of the ternary system has a definite angle of slope away from the predominant binary system. In this way the Alekseev rule makes it possible to examine the different relationships existing between the components and their mixtures in a ternary system.

4. A method was given for finding the predominant binary system from the character of the median line for the isotherm of immiscibility in a ternary system.

5. It was shown that a close bond exists between the character of conode distribution, the critical isothermal solution point and the median line, making it possible to describe the chemical activity taking place in a ternary system, beginning with any of these geometric elements.

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VISUAL-POLYTHERMAL STUDY OF THE SOLUBILITY OF THE SALTS IN THE RECIPROCAL SYSTEM COMPOSED OF POTASSIUM AND SODIUM NITRATES AND CHLORIDES AT 80, 100 and 125°

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A study of the quaternary reciprocal system composed of the nitrates and chlorides of potassium and sodium is of both great practical and theoretical interest.

The present work is part of an investigation on the chloride-nitrate exchange of the alkali and alkaline earth metals in aqueous solutions at temperatures approaching the joint boundary of solutions and anhydrous salt melts.

The solubility of the salts at our selected temperatures of 80, 100 and 125° was determined by the visual-polythermal method in the polythermostat of E. I. Akhumov and B. B. Vasilyev in sealed glass ampuls (1).

The boundaries of the concentration polyoctahedron of the system are the four ternary systems: KNO_3-KCl, $NaCl-NaNO_3$, $KCl-NaCl$ and KNO_3-NaNO_3 in the presence of water.

These systems have repeatedly been studied by both Soviet and foreign scientists. Thus, the system $NaNO_3-KNO_3-H_2O$ was studied by Carveth [2], D. J. Hissink [3], H. V. Briscoe and W. Madgin [4], G. Tammann and Ruppelt [5], F. I. Vasenin and A. G. Bergman [6], M. I. Ravich and F. G. Ginzberg [7], S. I. Aronova and Z. N. Lunskaya [8] and E. Janecke [9].

M. I. Ravish and F. G. Ginzberg were the first to give the complete polytherm for the system from the temperature of complete freezing to the fusion temperature of the components. It was established by the indicated authors that the solid solutions, formed between KNO_3 and $NaNO_3$ in the melts below 111.7°, i. e. below the temperature for the conversion KNO_3I-KNO_3II, are decomposed. The system $KNO_3-KCl-H_2O$ was studied by W. Reinders [10], Bodlander [11] and Barbaudy [12]. The system $NaCl-KCl-H_2O$ above 100° was studied by E. I. Akhumov and B. B. Vasilyev [13] and below 10° and up to the temperature of complete freezing by A. P. Palkin and E. N. Varasova [14]. The system $NaCl-NaNO_3-H_2O$ was studied by W. Reinders [10] and others. The quaternary reciprocal system composed of sodium and potassium nitrates and chlorides was also studied many times (W. Reinders [10], E. Cornec and H. Krombach [15], S. I. Aronova and Z. N. Lunskaya [8], and others).

In this work we give the results of our solubility studies, obtained by the visual-polythermal method [1], and only for the ternary systems $NaCl-NaNO_3-H_2O$ and $NaCl-KCl-H_2O$ were the compositions of the eutonic solutions taken after we had based our calculations on the data of W. Reinders [10] for the first system (258.7 moles of water per 100 moles of residual dry salts at 100 °), and those of E. I. Akhumov and B. B. Vasilyev [13] for the second system (640.00, 585.0 and 539.0 moles of water per 100 moles of residual dry salts at 80, 100 and 125°).

Our study results are given in the summary tables and depicted in the figures, characterizing the isothermal solubility in both the ternary boundary systems and in the reciprocal system as a whole (Tables 1-17, Figures 1-9).

From the data in Tables 3 and 4 it can be seen that chemism (chemical affinity) is not observed for the systems $KNO_3-KCl-H_2O$ and $NaCl-NaNO_3-H_2O$ in the temperature interval 80 - 125°.

TABLE 1

Solubility of the Salts in the System $KNO_3-KCl-H_2O$

System of salts	Amount of salts (in mole %)		80° Isotherm		100° Isotherm		125° Isotherm	
	KCl	KNO_3	Moles of H_2O per 100 moles of dry residue	Solid phases	Moles of H_2O per 100 moles of dry residue	Solid phases	Moles of H_2O per 100 moles of dry residue	Solid phases
KNO_3-H_2O	–	100.0	332.70	KNO_3	228.20	KNO_3	153.70	KNO_3
$KNO_3-KCl-H_2O$	3.36	96.6	310.41		225.80		148.90	
	2.90	90.10	307.73		223.88		136.70	
	16.22	83.98	295.99		214.33		158.30	
	19.31	80.69	287.12		218.22		177.70	
	22.36	77.64	297.44	KCl	224.90	KCl	191.1	KCl
	25.31	74.69	301.38		251.32		219.42	
	28.23	70.77	312.05		272.72		241.96	
	31.11	68.89	322.90		287.00		257.50	
	37.73	63.27	361.19		319.05		276.28	
	47.47	52.53	–		393.22		364.90	
	57.54	42.46	516.61		–		427.17	
	62.35	37.65	547.11		508.96		–	
	67.03	32.97	577.28		–		–	
	75.98	24.02	–		561.92		–	
$KCl-H_2O$	100.0	–	811.30		730.10		647.90	

TABLE 2

Composition of the Eutonic Solutions of the System $KNO_3-KCl-H_2O$

Isotherms	Amount of salts (in mole %)		Moles of H_2O per 100 moles of dry residue	Solid phases
	KNO_3	KCl		
80°	78.5	21.5	282.0	KNO_3 + KCl
100°	81.0	19.0	202.0	
125°	88.0	12.0	128.0	

The solubility data for the salts in the system $NaCl-KNO_3-H_2O$ (diagonal section) are given in Tables 5 and 6 and in Fig. 1. The 80, 100 and 125° solubility isotherms for this system intersect three fields – KNO_3, KCl and NaCl. With temperature elevation the KCl field increases due to increase in KNO_3 solubility.

On the basis of both literature and our own data the solubility isotherms for the salts in the system were projected on the composition squares, depicted in Figs. 7, 8 and 9.

The eutonic point of the solutions in the system $NaNO_3-KNO_3-H_2O$, and also the eutonic points of the reciprocal system for the studied isotherms were obtained by us graphically, by the method of projecting on a vertical plane the liquidus lines of the system $NaNO_3-KNO_3-H_2O$ and the liquidus lines for the joint crystallization of the two salt pairs: $NaNO_3-NaCl$ and KNO_3-KCl.

A study of the reciprocal system $Na^+, K^+ \| Cl^-, NO_3^- - H_2O$ in the temperature interval 80 –125° again confirmed the absence of chemical affinity between the individual components.

TABLE 3

Stability of the Salts in the System $NaCl-NaNO_3-H_2O$

System of salts	Amount of salts (in mole %)		80° Isotherm		100° Isotherm		125° Isotherm	
	NaCl	$NaNO_3$	Moles of H_2O per 100 moles of dry residue	Solid phases	Moles of H_2O per 100 moles of dry residue	Solid phases	Moles of H_2O per 100 moles of dry residue	Solid phases
$NaCl-NaNO_3-H_2O$	7.12	92.88	301.99	$NaNO_3$	–	$NaNO_3$	190.30	NaCl +
	13.90	86.10	288.91	$NaCl+NaNO_3$	265.39		238.02	$+NaNO_3$
	24.30	75.70	394.98	NaCl	380.25	NaCl	365.22	NaCl
$NaCl-H_2O$	100.0	–	854.40		829.16		805.16	
$NaNO_3-H_2O$	–	100.0	318.90	$NaNO_3$	271.50	$NaNO_3$	217.20	$NaNO_3$

TABLE 4

Composition of the Eutonic Solutions of the System $NaCl-NaNO_3-H_2O$

Isotherms	Amount of salts (In mole %)		Moles of H_2O per 100 moles of salts of dry residue	Solid phases
	NaCl	$NaNO_3$		
80°	15.0	85.0	288.91	$NaCl+NaNO_3$
100° *	12.0	88.0	253.90	
125°	9.0	91.0	190.30	

TABLE 5

Solubility of the Salts in the System $NaCl-KNO_3-H_2O$

System of salts	Amount of salts (in mole %)		80° Isotherm		100° Isotherm		125° Isotherm	
	NaCl	KNO_3	Moles of H_2O per 100 moles of dry residue	Solid phases	Moles of H_2O per 100 moles of dry residue	Solid phases	Moles of H_2O per 100 moles of dry residue	Solid phases
KNO_3-H_2O	–	100.0	332.70		228.20		153.70	KNO_3
$NaCl-KNO_3-H_2O$	8.34	91.66	291.71	KNO_3	208.15	KNO_3	119.42	
	15.93	84.07	260.75		181.70		120.80	
	23.36	76.64	248.82	KCl	192.05	KCl	170.27	KCl
	30.55	69.45	267.33		233.34		209.70	
	42.37	57.63	333.94		261.49	KCl + NaCl	231.76	KCl + NaCl
	42.57	57.43	–		300.89		–	
	48.20	51.80	369.90		351.61		334.22	
	63.36	–	518.62	NaCl	498.05		473.58	
	67.38	–	553.73		–	NaCl	–	NaCl
	80.14	–	658.88		637.29		619.81	
	90.73	–	771.90		745.49		–	
$NaCl-H_2O$	100.0		854.40		829.16		805.16	

* Data taken from Reinders [10].

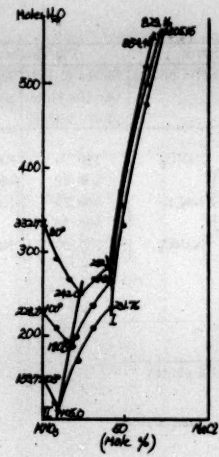

Figure 1. Solubility Isotherms of the system $NaCl-KNO_3-H_2O$
I – solutions, saturated with NaCl + KCl
II – solutions, saturated with KCl + KNO_3

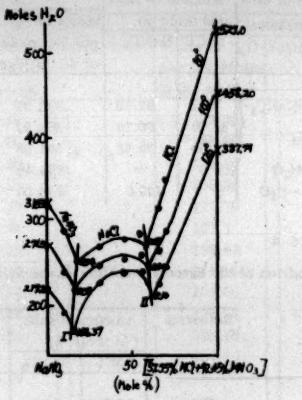

Figure 2. Internal section I [(57.55% KCl + 42.45% KNO_3) + $NaNO_3$] → H_2O
I – solutions, saturated with NaCl + $NaNO_3$
II – solutions, saturated with KCl + NaCl

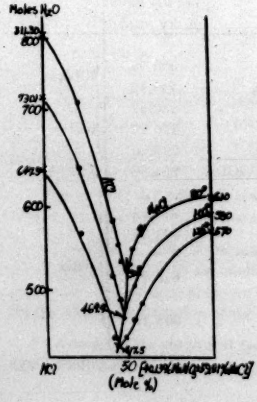

Figure 3. Internal section II [(40.19% $NaNO_3$ + 59.81% NaCl) + + KCl] → H_2O

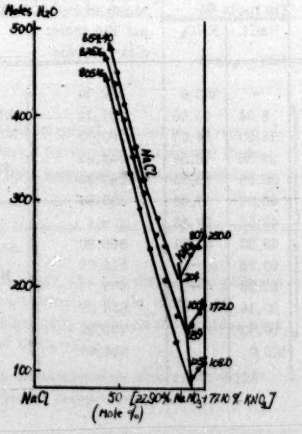

Figure 4. Internal section III [(22.90% $NaNO_3$ + 77.10% KNO_3) + + NaCl] → H_2O

TABLE 6

System $NaCl - KNO_3 - H_2O$ (Fig. 1)

Isotherms	Solution I				Solution II			
	Amount of salts (in mole %)		Moles of H_2O per 100 moles of dry residue	Solid phases	Amount of salts (in mole %)		Moles of H_2O per 100 moles of dry residue	Solid phases
	NaCl	KNO_3			NaCl	KNO_3		
80°	40.5	59.5	282.0	NaCl + KCl	25.0	75.0	242.0	KCl + KNO_3
100°	41.5	58.5	260.0		18.5	81.5	180.0	
125°	42.3	57.7	231.8		12.5	87.5	105.0	

TABLE 7

Internal section I [(57.55% KCl + 42.45% KNO_3) + $NaNO_3$] → H_2O

Systems of salts	Amount of salts (in mole %)		80° Isotherm		100° Isotherm		125° Isotherm	
	$NaNO_3$	KCl + KNO_3	Moles of H_2O per 100 moles of dry residue	Solid phases	Moles of H_2O per 100 moles of dry residue	Solid phases	Moles of H_2O per 100 moles of dry residue	Solid phases
(57.55%KCl + 42.45% KNO_3) + H_2O	–	100.0	527.00	KCl	458.20	KCl	387.79	KCl
[(57.55%KCl + 42.45% KNO_3) + $NaNO_3$] → H_2O	30.18	69.82	344.29		285.30		–	
	35.21	64.79	–		261.50		223.65	
	40.22	59.88	292.10		–		213.43	
	45.24	54.76	284.91	NaCl	259.00	NaCl	239.21	NaCl
	55.23	44.77	276.71		256.10		241.68	
	70.20	29.80	269.92		249.50		228.11	
	85.10	14.90	–		222.64		168.37	NaCl + $NaNO_3$
	90.07	9.93	284.00	$NaNO_3$	240.00	$NaNO_3$	190.00	
$NaNO_3 - H_2O$	100.0	–	318.00		271.5		217.2	$NaNO_3$

TABLE 8

Internal section I (Fig. 2)

Isotherms	Solution I				Solution II			
	Amount of salts (in mole %)		Moles of H_2O per 100 moles of dry residue	Solid phases	Amount of salts (in mole %)		Moles of H_2O per 100 moles of dry residue	Solid phases
	$NaNO_3$	KCl + KNO_3			$NaNO_3$	KCl + KNO_3		
80°	81.5	18.5	254	NaCl + $NaNO_3$	41.0	59.0	268.0	NaCl + KCl
100°	84.0	16.0	208		39.0	61.0	244.0	
125°	85.5	14.5	168.37		37.0	63.0	210.0	

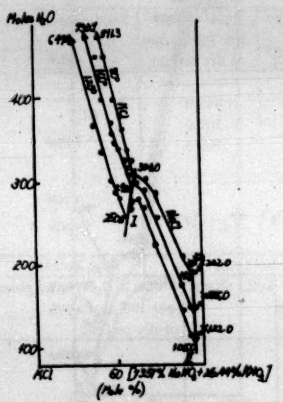

Figure 5. Internal section IV
[(73.51% $NaNO_3$ + 26.49% KNO_3) +
+ KCl] → H_2O.
I–solutions, saturated with NaCl + KCl,
II–solutions, saturated with NaCl + $NaNO_3$

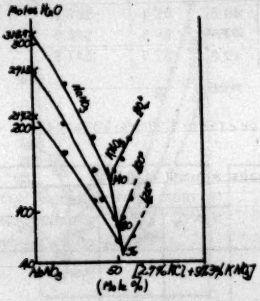

Figure 6. Internal section V
[(2.70% KCl + 97.30% KNO_3) +
+ $NaNO_3$] → H_2O.

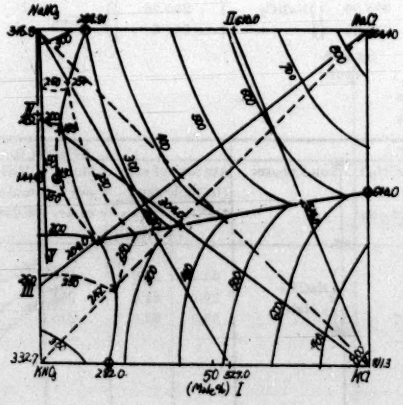

Figure 7. Projection of the 80° isotherms of the reciprocal system Na^+, K^+ || Cl^-, NO_3^- — H_2O

TABLE 9

Internal section II [(40.19% $NaNO_3$ + 59.81% NaCl) + KCl] → H_2O

System of salts	Amount of salts (in mole %)		80° Isotherm		100° Isotherm		125° Isotherm	
	KCl	($NaNO_3$ + NaCl)	Moles of H_2O per 100 moles of dry residue	Solid phases	Moles of H_2O per 100 moles of dry residue	Solid phases	Moles of H_2O per 100 moles of dry residue	Solid phases
(40.19% $NaNO_3$ +59.81% NaCl)+ H_2O	–	100.0	610.0	NaCl	590.0	NaCl	570.0	NaCl
[(40.19% $NaNO_3$ + 59.81% NaCl) + KCl] + H_2O	43.21	56.79	572.3		526.6		486.0	
	46.17	54.83	550.4		507.2		467.8	
	49.17	50.83	529.44				–	
	52.24	47.76	531.21	KCl	469.9	KCl+NaCl	425.0	KCl+NaCl
	55.19	44.81	554.0		490.2	KCl	417.5	
	58.40	41.60	584.5		516.9		444.4	KCl
	78.84	21.16	725.9		645.0		563.5	
KCl—H_2O	100.0	–	811.3		730.1		647.9	

TABLE 10

Internal section II. Composition of Solutions, Saturated with Several Salts

Isotherms	Amount of salts (in mole %)		Moles of H_2O per 100 moles of dry residue	Solid phases
	KCl	($NaNO_3$ +NaCl)		
80°	51.00	49.00	514.00	KCl + NaCl
100°	52.00	48.00	469.90	
125°	54.50	45.50	417.50	

TABLE 11

Internal Section III [(22.90% $NaNO_3$ + 77.10% KNO_3) + NaCl] → H_2O

Systems of salts	Amount of salts (in mole %)		80° Isotherm		100° Isotherm		125° Isotherm	
	NaCl	($NaNO_3$ + KNO_3)	Moles of H_2O per 100 moles of dry residue	Solid phases	Moles of H_2O per 100 moles of dry residue	Solid phases	Moles of H_2O per 100 moles of dry residue	Solid phases
(22.90% $NaNO_3$ +77.10% KNO_3) → H_2O	–	100.00	260.00	KNO_3	173.00	KNO_3	108.00	KNO_3
[(22.90% $NaNO_3$ + 77.10% KNO_3) + NaCl] → H_2O	3.37	96.63	251.30		166.30		102.42	
	9.06	90.94	235.30		152.00		94.21	
	11.89	88.11	–		139.00	KNO_3 +NaCl	98.19	
	15.62	84.38	211.20		164.60		130.80	
	22.71	77.29	226.30		204.90		–	
	29.39	70.61	277.90		252.50		240.60	
	35.71	64.29	324.40		306.70	NaCl	290.40	NaCl
	41.65	58.35	361.60	NaCl	350.10		333.30	
	47.28	52.72	413.30		397.10		–	
	52.62	47.38	453.80		440.30		402.40	
NaCl—H_2O	100.0	–	854.40		829.16		805.16	

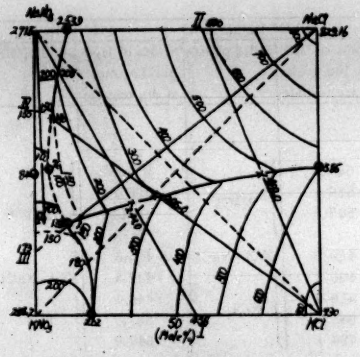

Fig. 8. Projection of the 100° Isotherm for the Reciprocal System Na^+, $K^+||Cl^-$, $NO_3^- - H_2O$

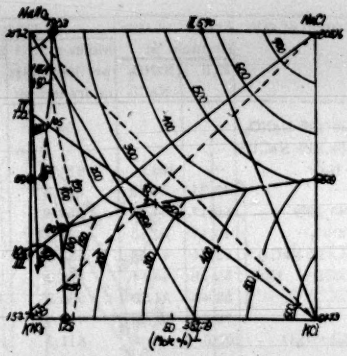

Fig. 9. Projection of the 125° Isotherms for the Reciprocal System Na^+, $K^+||Cl^-$, $NO_3^- - H_2O$

TABLE 12

Internal Section III. Composition of the Isothermal Solutions, Saturated with Several Salts

Isotherms	Amount of salts (in mole %)		Moles of H_2O per 100 moles of dry residue	Solid phases
	NaCl	($NaNO_3$ + KNO_3)		
80°	17.00	83.00	204.00	KNO_3 + NaCl
100°	12.00	88.00	139.00	
125°	11.00	89.00	90.00	

(See following page for Table 13)

TABLE 14

Internal Section IV (Fig. 5)

Isotherms	Solution I				Solution II			
	Amount of salts (in mole %)		Moles of H_2O per 100 moles of dry residue	Solid phases	Amount of salts (in mole %)		Moles of H_2O per 100 moles of dry residue	Solid phases
	KCl	($NaNO_3$ + KNO_3)			KCl	$NaNO_3$ + KNO_3		
80°	38.00	62.00	304.0	NaCl + KCl	6.50	93.5	183.0	NaCl + $NaNO_3$
100°	40.10	59.90	292.0		6.00	94.0	140.0	
125°	48.46	51.54	250.8		5.50	94.5	105.0	

TABLE 13

Internal Section IV [(73.51% $NaNO_3$ + 26.49% KNO_3) + KCl] → H_2O

Systems of salts	Amount of salts (in mole %)		80° Isotherm		100° Isotherm		125° Isotherm	
	KCl	($NaNO_3$ + KNO_3)	Moles of H_2O per 100 moles of dry residue	Solid phases	Moles of H_2O per 100 moles of dry residue	Solid phases	Moles of H_2O per 100 moles of dry residue	Solid phases
(73.51% $NaNO_3$ + 26.49% KNO_3)	–	100.0	204.00	$NaNO_3$	155.00	$NaNO_3$	122.00	$NaNO_3$
[(73.51% $NaNO_3$ + 26.49% KNO_3) + KCl] → H_2O	2.38	97.62	192.10		149.60		117.70	
	4.75	95.25	189.00		147.40		108.00	
	7.10	92.90	190.60	NaCl	148.50	NaCl	111.20	NaCl
	11.74	88.26	204.50		170.90		140.60	
	33.91	66.09	300.00		287.00		263.40	
	38.15	61.85	304.00		297.20		273.00	
	40.24	59.76	321.80		299.20	NaCl + KCl	272.80	
	42.32	57.68	323.30		307.60		266.80	
	44.38	55.62	336.30		312.20		250.80	
	46.44	53.56	359.90	NaCl + KCl	321.60		–	
	48.46	51.54	–		337.30		279.70	NaCl + KCl
	50.49	49.51	396.90		343.10	KCl	287.70	KCl
	52.50	47.50	397.80		356.00		308.90	
	54.47	45.53	–		369.30		332.20	
	58.43	41.57	448.30		397.50		338.10	
	64.23	35.77	587.20		–		344.90	
KCl – H_2O	100.00	–	811.30		730.10		647.90	

TABLE 15

Internal Section V [(2.70% KCl + 97.30% KNO_3) + $NaNO_3$] → H_2O

Systems of salts	Amount of salts (in mole %)		80° Isotherm		100° Isotherm		125° Isotherm	
	$NaNO_3$	KCl + KNO_3	Moles of H_2O per 100 moles of dry residue	Solid phases	Moles of H_2O per 100 moles of dry residue	Solid phases	Moles of H_2O per 100 moles of dry residue	Solid phases
[(KCl + KNO_3) + $NaNO_3$] → H_2O	44.04	55.96	182.74	KNO_3	112.23	KNO_3	70.78	KNO_3
	49.13	50.87	160.60		85.64		63.73	
	54.13	45.87	147.80		93.32		–	
	59.06	40.94	151.50		114.39		–	$NaNO_3$
	64.70	35.30	188.41	$NaNO_3$	150.30	$NaNO_3$	64.70	
	82.52	17.48	251.00		208.85		82.52	
$NaNO_3$ – H_2O	100.0	–	318.00		271.50		217.20	

TABLE 16

Internal Section V. Composition of Solutions, Saturated with Several Salts

Isotherms	Amount of salts (in mole %)		Moles of H_2O per 100 moles of dry residue	Solid phases
	$NaNO_3$	(KCl + KNO_3)		
80°	55.0	45.0	140.0	$NaNO_3$ + KNO_3
100°	50.0	50.0	80.0	
125°	47.5	52.5	56.0	

TABLE 17

Composition of the Eutonic Solutions for the Reciprocal System $Na^+, K^+ \| Cl^-, NO_3^- - H_2O$ at 80, 100 and 125°

Isotherms	Amount of salts (in mole %)			Moles of H_2O per 100 moles of dry residue	Solid phases
	NaCl	$NaNO_3$	KNO_3		
80°	5.94	56.00	38.06	130.00	$KNO_3 + NaNO_3 + NaCl$
100°	5.22	52.50	42.28	76.00	
125°	4.90	51.00	44.10	52.00	

When the 80, 100 and 125° isotherms (Figs. 7, 8 and 9) for the reciprocal system are compared, it can be noted that with elevation of the temperature the potassium nitrate field diminishes, i.e. the reaction for the conversion of sodium nitrate is directed toward increasing the potassium nitrate concentration in solution.

SUMMARY

1. The solubility of the salts in the reciprocal system composed of sodium and potassium chlorides and nitrates was studied at 80, 100 and 125° by the visual-polythermal method in sealed tubes.

2. On the basis of the obtained data the 80, 100 and 125° isotherms were constructed as projections on a square and 4 fields were outlined (KNO_3, KCl, NaCl and $NaNO_3$).

3. Chemical affinity between the components was not manifested in the system.

4. It was established that the potassium nitrate field is diminished when the temperature is raised to 125°.

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PHASE DIAGRAMS OF THE BINARY SYSTEMS MAGNESIUM CHLORIDE-ALKALI METAL CHLORIDES

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In the present paper we examine the rules observed for the changes in the phase diagrams of magnesium chloride-alkali metal chloride systems when successive transition from lithium to cesium is made.

Earlier [1], based on comprehensive experimental material, it was shown that a definite rule exists for the type of phase diagrams formed by binary systems. This made it possible to predict, in broad outlines, the form of the phase diagrams for systems still not studied.

EXPERIMENTAL

To make possible a comparison of the indicated systems we studied the phase diagrams of $RbCl-MgCl_2$ and $CsCl-MgCl_2$ in a specially constructed vertical tube electric furnace. The ceramic tube of the furnace had two openings, 25 mm. in diameter, to which quartz tubes were fastened, emerging from the furnace jacket and situated perpendicular to each other; one of these quartz tubes served for illumination, and the other for observations. A quartz cylinder, specially selected to fit the internal diameter of the tube, was placed inside the ceramic tube. The cylinder covered the opening and in that way prevented the escape of hot air from the furnace. The investigated mixture of salts was placed in a quartz test tube, which was mounted in the furnace cover in such fashion that its lower end was found against the observation opening. The quartz test tube was capped with a graphite cover having two openings, of which one opening served for introduction of the thermocouple, while the other served for the introduction of a porcelain tube, through which dry hydrogen chloride gas was passed into the melt. The furnace was warmed on top with a layer of asbestos wadding (having a thickness of 7 cm). The weight of salts taken for each experiment varied from 5 to 6 g, with such arrangement that the whole salt melt was visible to the observer.

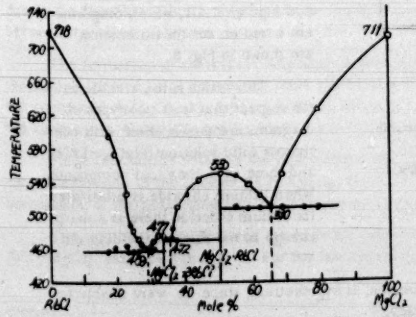

Fig. 1. Fusion Diagram of the System $RbCl-MgCl_2$.

The hydrogen chloride, dehydrated by means of phosphoric anhydride, was introduced even prior to the melting of the salts, and then was introduced into the melt for about an hour. In most cases the melts were completely clear; only for the melts with a high magnesium chloride content was some turbidity (suspension of MgO) noted at times, which, however, vanished with time as the result of hydrogen chloride passage. The hydrogen chloride flow was terminated during the time of measuring the temperature drops.

After the experiment the melt was poured into a warm porcelain dish; the solidified melt, still hot, was placed in a hermetically closed test tube and analyzed. The

amount of magnesium chloride was determined gravimetrically. The difference between the original composition and that found by analysis failed to exceed 0.5%. All of the compositions are expressed in mole percents.

The temperature was measured with a platinum–platinum-rhodium (Pt-PtRh) thermocouple.

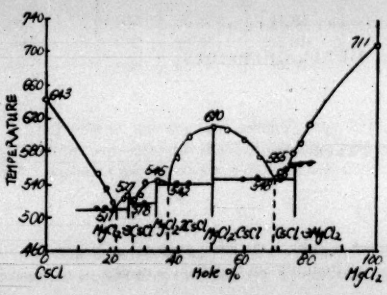

Fig. 2. Fusion Diagram of the System CsCl–$MgCl_2$

Anhydrous magnesium chloride was prepared in known manner from hydrous chemically pure magnesium chloride through ammonium carnallite. The $MgCl_2$ melting point was 711°. The rubidium chloride used was pure and had m. p. 718°; the cesium chloride used has m. p. 643°.

System RbCl–$MgCl_2$. The phase diagram of this system is characterized by two compounds that melt without decomposition: $RbMgCl_3$ at 550° and Rb_2MgCl_4 at 477° (Table 1, Fig. 1).

Eutectic points at: 1) 510° and 65% $MgCl_2$, 2) 472° and 35.5% $MgCl_2$, 3) 459° and 29% $MgCl_2$.

System CsCl–$MgCl_2$. The phase diagram of this system (Table 2, Fig. 2) is characterized by four compound components: compound $CsMg_3Cl_7$, stable below 565° and melting with decomposition; $CsMgCl_3$ with m. p. 610°; Cs_2MgCl_4 with m.p. 545° and Cs_3MgCl_5 with m. p. 527°.

Eutectic points at: 1) 548° and 69.4% $MgCl_2$, 2) 542° and 37% $MgCl_2$, 3) 518° and 26.5% $MgCl_2$, 4) 511° and 21.5% $MgCl_2$. In Fig. 2 a peritectic point exists at 565° and 73.5% $MgCl_2$, corresponding to the formation of the compound $CsMg_3Cl_7$,* which melts with decomposition.

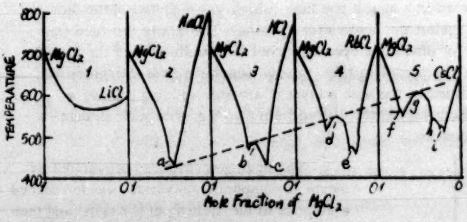

Fig. 3. Fusion Diagrams of the Systems

1) $MgCl_2$–LiCl (solid solutions) 2) $MgCl_2$–NaCl (a) compound $MgCl_2 \cdot NaCl$), 3) $MgCl_2$–KCl (b) compound $MgCl_2 \cdot KCl$, c) $MgCl_2 \cdot 2KCl$), 4) $MgCl_2$–RbCl (d) compound $MgCl_2 \cdot RbCl$, e) $MgCl_2 \cdot 2RbCl$) 5) $MgCl_2$–CsCl (f) $CsCl \cdot 3MgCl_2$, g) $MgCl_2 \cdot CsCl$, h) $MgCl_2 \cdot 2CsCl$, i) $MgCl_2 \cdot 3CsCl$).

When compared with the preceding system, it was revealed that two additional compounds were formed here, which compounds had the component ratios 1:3 and 3:1.

The phase diagrams of $MgCl_2$–LiCl [2], $MgCl_2$–NaCl [3], $MgCl_2$–KCl [4], $MgCl_2$–RbCl and $MgCl_2$–CsCl, which diagrams are based on our measurements, are shown in Fig. 3.

This series is remarkable in the respect that in it two types of diagrams are shown, those with continuous solid solutions ($MgCl_2$–LiCl), and those with chemical compounds. When lithium chloride is substituted for sodium chloride there is a sharp change in the form of the diagram.

* The composition of this compound melting with decomposition, is hypothetical, since we were unable to establish the duration of secondary rests with sufficient accuracy.

TABLE 1

System RbCl–$MgCl_2$

$MgCl_2$ (in mole %)	Start of first crystallization	Composition of the crystals	Start of crystallization for the Eutectics	Designation of the Eutectics
100	711°		–	
78.7	625		508°	
74.2	598	$MgCl_2$	509	
68.3	548		510	
(65.0)*	(510)		(510)	$MgCl_2$ + $RbMgCl_3$
64.5	512		–	
61.6	524		510	
58.1	536		509	
54.4	546		511	
(50.0)	(550)		–	
49.5	549	$RbMgCl_3$	–	
43.8	543		–	
40.1	525		–	
37.5	511		472	
36.2	486		473	$RbMgCl_3$ + Rb_2MgCl_4
(35.5)	(472)	–	(472)	
(33.3)	(477)		–	
33.1	476		–	
31.7	477	Rb_2MgCl_4	–	
30.4	470		460	
29.6	464		458	
(29.0)	(459)		(459)	
28.0	463		–	
27.1	468		–	
25.9	473		459	Rb_2MgCl_4 + RbCl
24.6	484		458	
23.7	491	RbCl	458	
22.7	527		464	
19.4	576		463	
17.5	595		458	
0	718		–	

due to the fact that lithium chloride, in its physicochemical properties, occupies an intermediate position between the alkali chlorides and the chlorides of the alkaline earth metals.

The formation of chemical compounds in the system $MgCl_2$ – NaCl is without doubt, but, as regards the composition of these compounds there exist contradictory opinions. Thus, according to the data of [3], the compound $NaMgCl_3$ (a), melting without decomposition, is formed, while according to the data of [5], the compounds $NaMg_2Cl_5$ and Na_2MgCl_4 are formed.

Since interaction between the components, leading to the formation of chemical compounds, is most clearly expressed in the systems KCl–$MgCl_2$, RbCl–$MgCl_2$ and CsCl–$MgCl_2$, it is of interest to make a comparison of the phase diagrams for these systems among themselves.

The liquidus curves between the extreme eutectic points for CsCl–$MgCl_2$, RbCl – $MgCl_2$ and KCl–$MgCl_2$ are shown in Fig. 4. For the last system the liquidus lines are plotted from the data of [4].

* The figures shown in parentheses were obtained graphically.

TABLE 2

System CsCl–$MgCl_2$

$MgCl_2$ (in mole %)	Srart of first crystallization	Composition of the crystals	Start of crystallization for the Eutectics	Designation of the Eutectics	Start of crystallization for the Compounds	Composition of the compounds
100	711°	$MgCl_2$	–	–	567°	$CsMg_3Cl_7$
79.4	614		–	–	565	
76.6	589		–	–	564	
74.4	578		–	–	(565)	
(73.5)	(565)*		–	–	–	–
72.4	558		–	–	–	–
71.9	551	–	–	–	–	–
70.8	554	–	546°	$CsMgCl_3 + CsMg_3Cl_7$	–	–
69.4	548	–	548		–	–
64.3	575	$CsMgCl_3$	548	$CsMgCl_3 + CsMg_3Cl_7$	–	–
59.5	594		548		–	–
54.6	606		–	–	–	–
(50.0)	(610)		–	–	–	–
49.9	610		–	–	–	–
43.0	598		543		–	–
39.2	573		542	$CsMgCl_3 + Cs_2MgCl_4$	–	–
(37.0)	(542)		(542)		–	–
33.4	545	Cs_2MgCl_4	–	–	–	–
30.0	542		518		–	–
28.5	528		–	$Cs_2MgCl_4 + Cs_3MgCl_5$	–	–
26.7	523		–		–	–
(26.5)	(518)		(518)		–	–
(25.0)	(527)	Cs_3MgCl_5	–	–	–	–
24.4	527		–	–	–	–
23.6	523		–	–	–	–
(21.5)	(511)		(511)		–	–
20.3	518	CsCl	510	$Cs_3MgCl_5 + CsCl$	–	–
18.0	535		512		–	–
15.2	552		512		–	–
0	643		–	–	–	–

In Fig. 4 the following attract attention.

1. The eutectic points, situated on the magnesium chloride side, fall almost on a straight line (BDE). The paths for the crystallization of $MgCl_2$ in the presence of CsCl, RbCl and KCl almost merge (among themselves).

2. The eutectic points, situated on the side of the chlorides of potassium, rubidium and cesium, and the eutectic points, marking the limits of compounds of type $MeMgCl_3$ and $MeMgCl_4$, are also located on straight lines (lines AG and BG, Fig. 4).

3. The melting point of the compound $RbMgCl_3$ (550°) exceeds the melting point of the compound

* The figures shown in parentheses were obtained graphically.

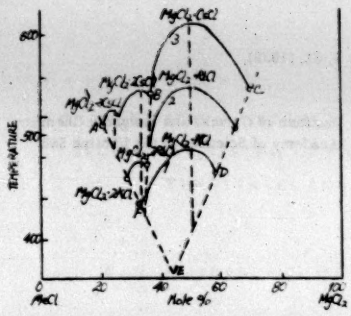

Fig. 4. Portions of the Liquidus Curves in the Systems 1) $MgCl_2$–KCl, 2) $MgCl_2$–RbCl, 3) $MgCl_2$–CsCl. Explanation in the text

$KMgCl_3$ (490°) by 60°, while the melting point of $CsMgCl_3$ (610°) exceeds that of $RbMgCl_3$ also by 60° (Fig. 3).

Consequently, the stability of the chemical compound increases in regular fashion in going from potassium to cesium, although the melting points of the corresponding alkali metal chlorides decrease.

A conclusion as to the probable compounds present in the system $MgCl_2$–NaCl can be obtained from Fig. 4. If the sector ABG is regarded as a region in which compounds of type Me_2MgCl_4 should appear, then there is no room for Na_2MgCl_4, since the extreme position has been occupied by K_2MgCl_4 (already showing appreciable decomposition in the solid state [4]).

If the portion EGBVD is regarded as a region in which compounds of the type of carnallite $MeMgCl_3$–should appear, then the existence of the compound $NaMgCl_3$ is fully admissible, which agrees with the phase diagram of [3], but fails to agree with the diagram of [5].

The increasing tendency for complex formation in going from lithium to cesium stands out with special clearness for the chlorides of magnesium and the alkali metals, which, undoubtedly, is associated with the dimensions of the alkali metal ions.

Since in this case magnesium emerges as a complex-former, forming anionic complexes (which was proven, for example, by measuring the transfer numbers [6]), a weakening of the ionic field for the alkali metal (with increase in the ionic radius) serves to facilitate shielding of the magnesium by the chlorine ions and, consequently, the formation of the anionic complex.

In accord with this, in the system KCl–$MgCl_2$ only the compound $KMgCl_3$ is stable; in the system RbCl–$MgCl_2$ already two compounds, $RbMgCl_3$ and Rb_2MgCl_4 are stable, while in the system CsCl–$MgCl_2$ three compounds are stable: $CsMgCl_3$, Cs_2MgCl_4 and Cs_3MgCl_5.

The authors are grateful to Yu. K. Delimarsky for his cooperation in the execution of the present work.

SUMMARY

1. The fusion of the systems RbCl–$MgCl_2$ and CsCl–$MgCl_2$ was studied by the visual-polythermal method. Two compounds, melting without decomposition, are formed in the system RbCl–$MgCl_2$: $RbMgCl_3$ and Rb_2MgCl_4; in the system CsCl–$MgCl_2$ three compounds are formed: $CsMgCl_3$, Cs_2MgCl_4, Cs_3MgCl_5, and one compound, $CsMg_3Cl_7$, melting with decomposition.

2. A definite rule is observed in the change of the phase diagrams when potassium is substituted for rubidium and rubidium for cesium: the crystallization of the compounds extends over a constantly greater composition region, while the crystallization temperature of the compounds steadily rises.

3. A weakening of the ionic field for the alkali metal (with increase in the ionic radius) favors complex formation. If magnesium chloride forms one stable compound with potassium chloride, then with rubidium chloride it forms two, and with cesium chloride it forms three compounds.

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EXCHANGE DECOMPOSITION IN THE ABSENCE OF A SOLVENT
RECIPROCAL SYSTEM OF POTASSIUM AND LITHIUM
TUNGSTATES AND METABORATES

A. G. Bergman, A. I. Kislova and V. I. Posypaiko

A study of the given system is a problem of studying a series of reciprocal systems with participation of the tungstates of potassium and lithium, forming a binary salt complex of the type $K_2WO_4 \cdot Li_2WO_4$.

The absence of data on the heats of formation for potassium and lithium tungstates, and also for the compounds, formed in the studied system Li, K $\| WO_4, BO_2$, render void the possibility of calculating the conditional thermochemical effect for the exchange [1] and complex-formation reactions, and consequently, the ability to predict the direction of the exchange reaction and the general form of the phase diagram.

EXPERIMENTAL

Method of Operation and Reagents. The system was studied by the visual-polythermal method. The melting points of the purified salts were: K_2WO_4 926°, KBO_2 947°, Li_2WO_4 738°, polymorphous transformation at 660°, and $LiBO_2$ 843°. In the tables are given the minimum number of points, needed to construct the fusion curves; they are given in their entirety in the figures.

Binary Systems. 1. $K_2(BO_2)_2 - Li_2(BO_2)_2$ (Fig. 1, Table 1) consists of three branches: α and β $Li_2(BO_2)_2$ and $K_2(BO_2)_2$, intersecting at 794° and 11% $K_2(BO_2)_2$ and at 582° and 56% $Li_2(BO_2)_2$.

2. $Li_2WO_4 - Li_2(BO_2)_2$ (Fig. 1, Table 1). The fusion curve consists of four branches: α and β $Li_2(BO_2)_2$, and compounds $3Li_2WO_4 \cdot 2LiBO_2$ and α Li_2WO_4. The side compound of composition $3Li_2WO_4 \cdot 2LiBO_2$* melts with decomposition; its composition was made exact on the basis of studying the system $Li_2SO_4 - Li_2(BO_2)_2$, in which the compound $3Li_2SO_4 \cdot 2LiBO_2$ is formed, melting without decomposition at 742°. The transition point corresponds to 710° and 19 % $Li_2(BO_2)_2$ and the eutectic point to 686° and 8% $Li_2(BO_2)_2$. The transition point for the α and β forms of $Li_2(BO_2)_2$ is fixed at 814° and 87.5 % $Li_2(BO_2)_2$.

3. $Li_2WO_4 - K_2WO_4$ (Fig. 1, Table 1) was studied earlier by van Liempt [3]. The investigation of the liquidus was repeated by one of us and the presence of the compound $Li_2WO_4 \cdot K_2WO_4$*, having a 1 : 1 composition, was confirmed (with a distinct maximum at 626°). The eutectic points of the system are at 560° and 33.5% K_2WO_4 and 572° and 63.5% K_2WO_4.

4. $K_2WO_4 - K_2(BO_2)_2$ (Fig. 1, Table 1). The liquidus consists of two branches: K_2WO_4 and $K_2(BO_2)_2$ with eutectic at 808° and 40% $K_2(BO_2)_2$.

Stable Diagonal Section $K_2WO_4 - Li_2(BO_2)_2$ (Fig. 2, Table 2). A binary system with eutectic point at 670° and 47% $Li_2(BO_2)_2$ and having an inversion point within the system. Transition of the α and β $Li_2(BO_2)_2$ at 774° and 85 % $Li_2(BO_2)_2$.

* From here on and in the figures: $Li_2WO_4 \cdot K_2WO_4 - D_1$, $3Li_2WO_4 \cdot 2LiBO_2 - D_2$.

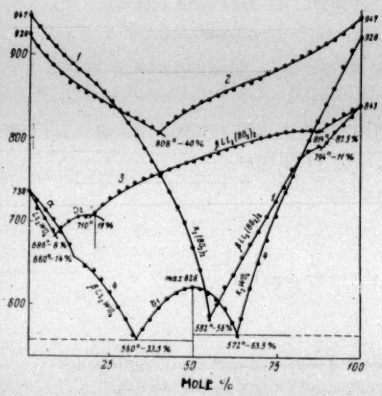

Fig. 1. Binary Systems
1) $K_2(BO_2)_2 - Li_2(BO_2)_2$, 2) $K_2WO_4 - K_2(BO_2)_2$
3) $Li_2WO_4 - Li_2(BO_2)_2$, 4) $Li_2WO_4 - K_2WO_4$

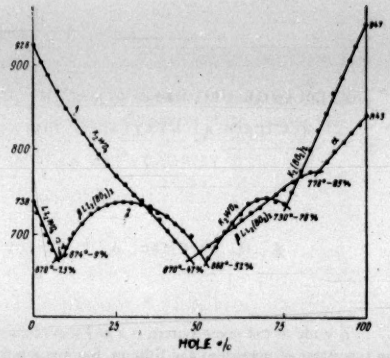

Fig. 2. Diagonal Sections
1) $K_2WO_4 - Li_2(BO_2)_2$, 2) $Li_2WO_4 - K_2(BO_2)_2$.

TABLE 1

Binary Systems

$K_2(BO_2)_2 - Li_2(BO_2)_2$		$Li_2WO_4 - Li_2(BO_2)_2$		$Li_2WO_4 - K_2WO_4$		$K_2WO_4 - K_2(BO_2)_2$	
$Li_2(BO_2)_2$ (in mole %)	t°	$Li_2(BO_2)_2$ (in mole %)	t°	K_2WO_4 (in mole %)	t°	$K_2(BO_2)_2$ (in mole %)	t°
0.0	947	0.0	738	0.0	738	0.0	926
5.0	920	2.5	718	5.0	716	5.0	898
10.0	900	5.0	710	10.0	690	10.0	878
15.0	884	7.5	694	12.5	678	15.0	862
25.0	846	10.0	694	15.0	656	20.0	852
35.0	790	12.5	704	20.0	644	25.0	840
45.0	718	15.0	710	25.0	618	30.0	830
50.0	672	17.5	710	30.0	586	35.0	820
55.0	590	20.0	716	32.5	566	40.0	808
57.5	604	22.5	724	35.0	574	45.0	826
60.0	624	25.0	730	40.0	600	50.0	840
65.0	660	30.0	744	45.0	618	55.0	848
70.0	692	40.0	762	50.0	626	60.0	856
75.0	728	50.0	776	55.0	618	65.0	864
80.0	764	60.0	790	60.0	600	70.0	872
85.0	790	70.0	804	62.5	582	75.0	884
87.5	794	80.0	814	65.0	588	80.0	894
90.0	798	85.0	814	70.0	654	85.0	905
92.5	810	87.5	814	80.0	760	90.0	916
95.0	820	90.0	820	90.0	846	95.0	926
100.0	843	100.0	843	100.0	926	100.0	947

TABLE 2

Diagonal Sections

$K_2WO_4-Li_2(BO_2)_2$				$Li_2WO_4-K_2(BO_2)_2$			
$Li_2(BO_2)_2$ (in mole %)	t°	$Li_2(BO_2)_2$ (in mole %)	t°	$K_2(BO_2)_2$ (in mole %)	t°	$K_2(BO_2)_2$ (in mole %)	t°
0.0	926	55.0	692	0.0	738	50.0	678
5.0	890	60.0	708	1.0	724	52.5	670
10.0	850	65.0	722	2.5	710	55.0	684
15.0	820	70.0	738	3.5	700	60.0	712
20.0	796	75.0	752	5.0	690	70.0	740
25.0	770	80.0	770	6.0	680	75.0	734
30.0	748	85.0	774	7.5	670	77.5	750
35.0	730	87.5	786	8.0	672	80.0	774
40.0	704	90.0	795	9.0	674	90.0	866
42.5	690	100.0	843	10.0	684	100.0	947
45.0	680			11.5	694		
47.5	670			12.5	700		
50.0	678			13.5	704		
				15.0	712		
				20.0	730		
				25.0	736		
				30.0	736		
				35.0	730		
				40.0	720		
				45.0	705		

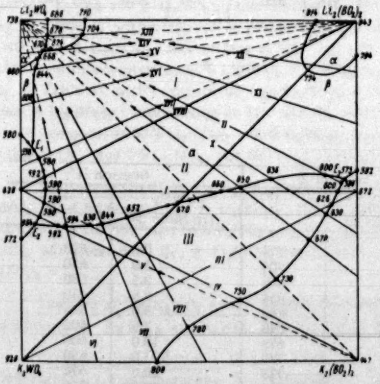

Fig. 3. Direction of the Internal Sections of the Systems

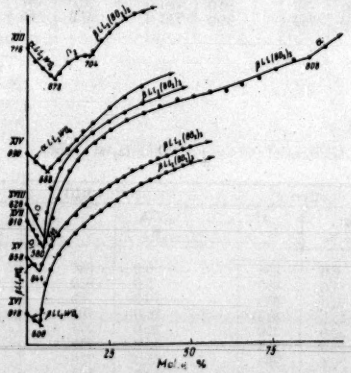

Fig. 4. Internal Sections of the Systems at the $Li_2(BO_2)_2$ Apex.

Metastable Diagonal Section $Li_2WO_4-K_2(BO_2)_2$ (Fig. 2, Table 2). Has 5 branches: Li_2WO_4, $K_2(BO_2)_2$ and exchange products D_2 β $Li_2(BO_2)_2$ and K_2WO_4.

Composition and temperature of the intersection points of the branches: Li_2WO_4 and D_2 – 670° and 7.5% $K_2(BO_2)_2$; D_2 and β $Li_2(BO_2)_2$ – 674° and 9% $K_2(BO_2)_2$; β $Li_2(BO_2)_2$ and K_2WO_4 – 666° and 52% $K_2(BO_2)_2$; K_2WO_4 and $K_2(BO_2)_2$ – 730° and 76% $K_2(BO_2)_2$.

Stable Section XVIII. 50% K_2WO_4 + 50% Li_2WO_4–$Li_2(BO_2)_2$ (Fig. 4, Table 3), is a binary system with an inversion eutectic point at 592° and 7% $Li_2(BO_2)_2$.

Internal Sections. Eighteen internal sections were studied (Fig. 3, Tables 3, 4 and 5).

Sections at the $Li_2(BO_2)_2$ Apex. Section XIII (Fig. 4, Table 3) with composition 95% Li_2WO_4 + 5% K_2WO_4 has 3 branches: α Li_2WO_4, $2Li_2WO_4 \cdot LiBO_2$ and β $Li_2(BO_2)_2$, intersecting at 678° and 8% $Li_2(BO_2)_2$ and 704° and 19% $Li_2(BO_2)_2$. Section XIV (Fig. 4, Table 3) with composition 90% Li_2WO_4 + 10% K_2WO_4 has 2 branches α Li_2WO_4 and β $Li_2(BO_2)_2$, intersecting at 668° and 6.5% $Li_2(BO_2)_2$. Section XV (Fig. 4, Table 3) with composition 85% Li_2WO_4 + 15% K_2WO_4 has 2 branches β Li_2WO_4 and β $Li_2(BO_2)_2$, intersecting at 644° and 4% $Li_2(BO_2)_2$. Section XVI (Fig. 4, Table 3) with composition 75% Li_2WO_4 + 25% K_2WO_4, has 2 branches: β Li_2WO_4 and β $Li_2(BO_2)_2$, intersecting at 606° and 3.5% $Li_2(BO_2)_2$. Section XVII (Fig. 4, Table 3) with composition 60% Li_2WO_4 + 40% K_2WO_4 has 2 branches: β Li_2WO_4 and β $Li_2(BO_2)_2$, intersecting at 580° and 5% $Li_2(BO_2)_2$.

TABLE 3

Internal Sections at the $Li_2(BO_2)_2$ Apex.

Section XIII		Section XIV		Section XV		Section XVI		Section XVII		Section XVIII	
$Li_2(BO_2)_2$ (in mole %)	t°	$Li_2(BO_2)_2$ (in mole %)	t°	$Li_2(BO_2)_2$ (in mole %)	t°	$Li_2(BO_2)_2$ (in mole %)	t°	$Li_2(BO_2)_2$ (in mole %)	t°	$Li_2(BO_2)_2$ (in mole %)	t°
0.1	716	0.0	690	0.5	658	0.0	618	0.0	610	0.0	620
5.0	690	2.5	680	2.5	650	2.5	610	1.5	600	5.0	598
7.5	684	5.0	674	5.0	650	4.0	608	2.5	592	7.5	610
10.0	684	7.5	674	7.5	672	4.5	620	3.5	586	10.0	652
15.0	704	10.0	682	10.0	684	5.0	650	5.0	586	20.0	700
17.5	704	15.0	704	15.0	710	7.5	670	6.0	620	40.0	744
20.0	710	20.0	724	20.0	730	10.0	684	7.5	650	60.0	766
25.0	734	25.0	744	25.0	744	15.0	710	10.0	672	80.0	804
30.0	750	30.0	756	30.0	754	20.0	730	20.0	715	85.0	808
35.0	760	35.0	770	35.0	766	30.0	756	30.0	736	90.0	824

TABLE 4

Internal Sections of the System at the Li_2WO_4 Apex

Section VI		Section VIII		Section X		Section II	
Li_2WO_4 (in mole %)	t°	Li_2WO_4 (in mole %)	t°	Li_2WO_4 (in mole %)	t°	Li_2WO_4 (in mole %)	t°
0.0	854	0.0	846	0.0	774	0.0	672
5.0	850	5.0	810	5.0	704	1.0	650
10.0	840	10.0	780	10.0	636	2.5	630
15.0	824	15.0	780	15.0	654	3.5	610
20.0	790	20.0	774	20.0	660	5.0	586
25.0	754	30.0	750	25.0	640	7.5	600
30.0	704	35.0	726	30.0	678	10.0	600
35.0	660	40.0	689	40.0	720	15.0	650
40.0	600	45.0	660	45.0	738	20.0	676
50.0	642	50.0	680	50.0	746	30.0	718

Sections at the Li_2WO_4 Apex. Section VI (Fig. 5, Table 4) with composition 80% K_2WO_4 + 20% $K_2(BO_2)_2$ has two branches: K_2WO_4 and β $Li_2(BO_2)_2$, intersecting at 594° and 40% Li_2WO_4. Section VII (Fig. 5, Table 4) with composition 60% K_2WO_4 + 40% $K_2(BO_2)_2$ consists of two branches: K_2WO_4 and β $Li_2(BO_2)_2$ intersecting at 644° and 40.5% Li_2WO_4. Section VIII (Fig. 5, Table 4) with composition 45% K_2WO_4 + 55% $K_2(BO_2)_2$ consists of

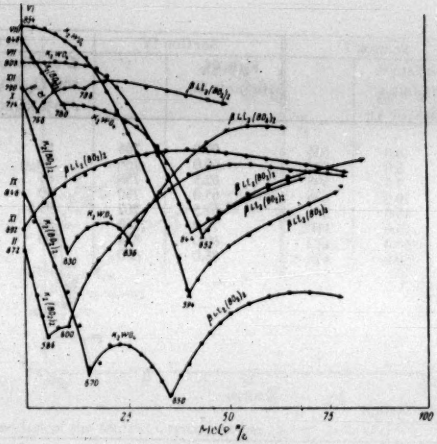

Fig. 5. Internal Sections of the System at the Li_2WO_4 Vertex

three branches: $K_2(BO_2)_2$, K_2WO_4 and β $Li_2(BO_2)_2$, intersecting at 780° and 10% Li_2WO_4 and 562° and 42.5% Li_2WO_4. Section IX (Fig. 5, Table 4) with composition 25% $Li_2(BO_2)_2$ + 75% $K_2(BO_2)_2$ consists of three branches $K_2(BO_2)_2$, K_2WO_4 and β $Li_2(BO_2)_2$, intersecting at 670° and 15% Li_2WO_4 and 650° and 35% Li_2WO_4. Section X (Fig. 5, Table 4) with composition 37.5% $Li_2(BO_2)_2$ + 62.5% $K_2(BO_2)_2$ consists of three branches: $K_2(BO_2)_2$, K_2WO_4 and β $Li_2(BO_2)_2$, intersecting at 630° and 10% Li_2WO_4, and 636° and 25% Li_2WO_4. Section XI (Fig. 5, Table 4) with composition 70% $Li_2(BO_2)_2$ + 30% $K_2(BO_2)_2$ consists of one branch: β $Li_2(BO_2)_2$. Section XII (Fig. 5, Table 4) with composition 85% $Li_2(BO_2)_2$ + 15% $K_2(BO_2)_2$ consists of three branches: β, α and again β $Li_2(BO_2)_2$, intersecting at 766° and 4% Li_2WO_4 and 786° and 16% Li_2WO_4. Section II (Fig. 5, Table 4) with composition 50% $Li_2(BO_2)_2$ + 50% $K_2(BO_2)_2$ has 3 branches: $K_2(BO_2)_2$, K_2WO_4 and β $Li_2(BO_2)_2$, intersecting at 586° and 5% Li_2WO_4 and 600° and 10% Li_2WO_4.

Sections at the $K_2(BO_2)_2$ Apex. Section IV (Fig. 6, Table 5) with composition 50% Li_2WO_4 + 50% K_2WO_4 has 4 branches: D_2, β $Li_2(BO_2)_2$, K_2WO_4 and $K_2(BO_2)_2$, intersecting at 590° and 7% $K_2(BO_2)_2$, 630° and 20% $K_2(BO_2)_2$ and 750° and 64% $K_2(BO_2)_2$. Section V (Fig. 6, Table 5) with composition 42.5% Li_2WO_4 + 57.5% K_2WO_4 has 3 branches D_1, β $Li_2(BO_2)_2$ and K_2WO_4, intersecting at 580° and 5.5% $K_2(BO_2)_2$ and 592° and 10% $K_2(BO_2)_2$.

Sections at the K_2WO_4 Apex. Section III (Fig. 6, Table 5) with composition 50% $Li_2(BO_2)_2$ + 50% $K_2(BO_2)_2$ has 2 branches: $K_2(BO_2)_2$ and K_2WO_4, intersecting at 626° and 9% K_2WO_4.

Cross-Section. Section I (Fig. 6, Table 5) with composition 50% Li_2WO_4 + 50% K_2WO_4 [50% $Li_2(BO_2)_2$ + 50% $K_2(BO_2)_2$], has 4 branches: D_1, β $Li_2(BO_2)_2$, K_2WO_4 and $K_2(BO_2)_2$ intersecting at 590° and 7% of 50% $Li_2(BO_2)_2$ + 50% $K_2(BO_2)_2$ and 660° and 60% of the same mixture, and at 600° and 93.5% of the same mixture of salts.

Crystallization Surface of the System. As a result of studying the binary sides, the diagonals and the 18 internal sections, the three-dimensional phase diagram of the reciprocal system was constructed by projection on the composition square (Fig. 7).

The surface of the liquidus consists of six fields and one additional field, which field is conditioned by the presence of polymorphism for lithium metaborate.

TABLE 5

Internal Sections of the System

Section IV		Section I		Section IV		Section I	
$K_2(BO_2)_2$ (in mole %)	t°	% of Mixture: 50% $Li_2(BO_2)_2$ + 50% $K_2(BO_2)_2$	t°	$K_2(BO_2)_2$ (in mole %)	t°	% of Mixture: 50% $Li_2(BO_2)_2$ + 50% $K_2(BO_2)_2$	t°
0.0	626	0.0	626	50.0	766	60	660
5.0	597	5.0	598	60.0	766	70	660
7.5	597	7.5	598	62.5	758	85	646
12.5	624	10.0	636	65.0	750	90	630
17.5	640	15.0	660	67.5	762	92.5	610
20.0	632	25.0	680	70.0	780	95	610
25.0	674	40.0	682	80.0	854	100	672
35.0	734	50.0	678	85.0	860		

TABLE 6

Area Dimensions of the Fields in the System

Fields	Crystallization Field	Area (in %)
1	Potassium metaborate	14.76
2	Potassium tungstate	32.63
3	Double lithium and potassium tungstate	1.59
4	Lithium tungstate:	
	α−modification	0.95
	β−modification	0.94
5	Field of compound D_2	0.88
6	Lithium metaborate:	
	α−modification	46.06
	β−modification	2.19

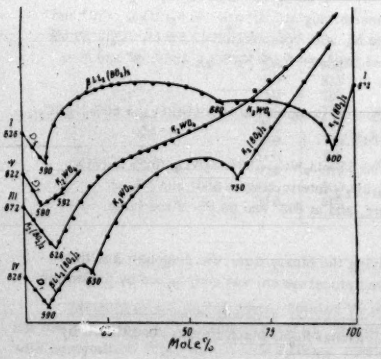

Fig. 6. Internal Sections of the System at the $K_2(BO_2)_2$ and K_2WO_4 Vertexes.

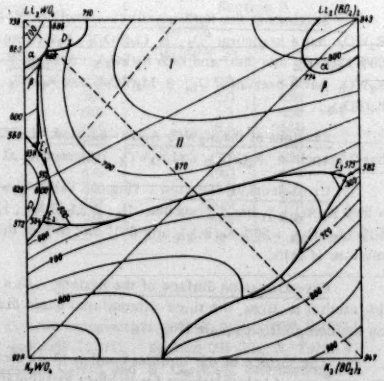

Fig. 7. Projection of the Surface of Crystallization for the System on a Square Base.

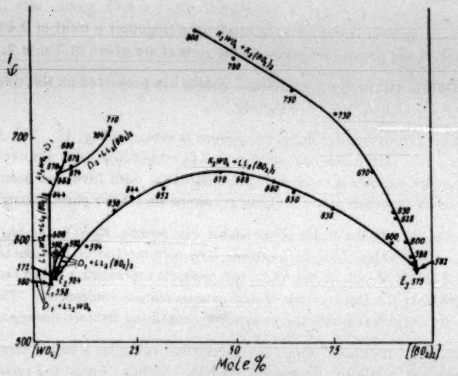

Fig. 8. Projection of the Mutual Crystallization Curves on the $K_2WO_4-K_2(BO_2)_2$ Side. Explanation in the text.

TABLE 7

Point	Character of Point	t°	Composition (in mole %)				Equilibrium Phases
			K_2WO_4	$Li_2(BO_2)_2$	Li_2WO_4	$K_2(BO_2)_2$	
E_1	Eutectic	558	40	5	55		β-Li_2WO_4—β-$Li_3(BO_2)_3$—D_1
E_2	Eutectic	564	60	4	36		D_1—K_2WO_4—β-$Li_3(BO_2)_3$
E_3	Eutectic	575	4	54	—	42	K_2WO_4—β-$Li_3(BO_2)_3$—$K_3(BO_2)_3$
P	Transition	668	10	7.5	82.5		Li_2WO_4—β-$Li_3(BO_2)_3$—D_2

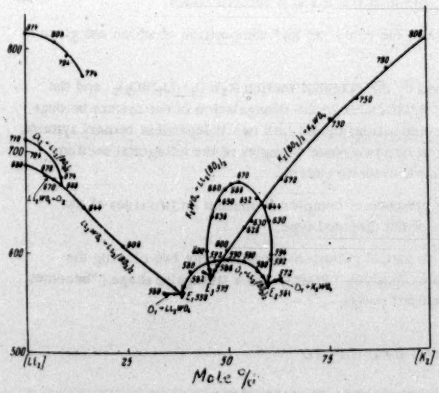

Fig. 9. Projection of the Mutual Crystallization Curves on the $Li_2WO_4-K_2WO_4$. Explanation in the text.

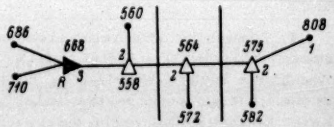

Fig. 10. Scheme of the Crystallization Tree for the Reciprocal System.
1) eutectic of the binary system,
2) ternary eutectic point,
3) ternary transition point (R).

The area dimensions of the fields, expressed in weight percents of the total area of the composition square, are given in Table 6.

The fields of both of the complexes occupy a very small area (together a total of 2.47% of the composition square area). The compositions of the nonvariant points in the system are given in Table 7.

The curves of mutual crystallization in the reciprocal system are projected on the side of the composition square: $K_2WO_4-K_2(BO_2)_2$ (Fig. 8) and $Li_2WO_4-K_2WO_4$ (Fig. 9).

The scheme of the crystallization tree for the given system is shown in Fig. 10. The system is an irreversible-reciprocal system with a stable diagonal section $K_2WO_4-Li_2(BO_2)_2$ with a eutectic point with inversion at 670°, and the subordinate adiagonal section [2] $D_1-Li_2(BO_2)_2$ with inversion point at 592°. These two sections divide the (composition) square of the reciprocal system into three phase triangles.

On the surface of crystallization in the fields of the stable components K_2WO_4 and $Li_2(BO_2)_2$ we see a sharp deviation of the ridges in their fields of crystallization. The intersection by the metastable diagonal section $Li_2WO_4-K_2(BO_2)_2$ of the fields of both of the exchange products represents a more rare case when compared with the usual type where only the fields of one stable component are intersected. This characteristic type (of intersection) is met with especial frequence in systems containing lithium compounds.

The complex $Li_2WO_4 \cdot K_2WO_4$, melting without decomposition, occupies a small portion on the (composition) square of the reciprocal system, while the compound $3Li_2WO_4 \cdot 2LiBO_2$, inside the system, and disappearing in a transition point, occupies an even smaller portion.

Thus, we see that in the given system the exchange equilibrium sharply dominates over the reactions of complex formation.

SUMMARY

1. The liquidus curves for the three binary systems $Li_2(BO_2)_2-K_2(BO_2)_2$, $K_2(BO_2)_2-K_2WO_4$ and $Li_2WO_4-Li_2(BO_2)_2$, defining the limits of the composition square for the reciprocal system Li, K $\|$ WO_4, BO_2, were studied for the first time; the first two are eutectic curves, while in the third we were the first to establish the presence of the compound $3Li_2WO_4 \cdot 2LiBO_2$, melting with decomposition and having a transition point at 710° and 19% $Li_2(BO_2)_2$.

2. The surface of crystallization for the reciprocal system Li, K $\|$ WO_4, BO_2 consists of six fields, of which two are fields of the complex compounds $Li_2WO_4 \cdot K_2WO_4$ and $3Li_2WO_4 \cdot 2LiBO_2$. The lithium tungstate and lithium metaborate fields are divided into portions containing the α and β modifications.

3. Four nonvariant points are contained in the system, the character and composition of which are given in Table 8.

4. Triangulation of the reciprocal system is realized by the diagonal section $K_2WO_4-Li_2(BO_2)_2$ and the adiagonal section $Li_2WO_4 \cdot K_2WO_4-Li_2(BO_2)_2$. Decisive significance in the triangulation of the system belongs to the diagonal section $K_2WO_4-Li_2(BO_2)_2$, dividing the (composition) square into two independent ternary systems, one of which in turn is subjected to secondary triangulation into two phase triangles of the adiagonal section $Li_2WO_4 \cdot K_2WO_4-Li_2(BO_2)_2$, bearing the character of a simple eutectic system.

As a result the given reciprocal system, despite the presence of complex formation on two sides of the (composition) square, is an irreversible-reciprocal system of the diagonal type.

5. Under the influence of lithium metaborate and in part of potassium tungstate, the two playing the part of salt solvents, the crystallization field of the complex $3Li_2WO_4 \cdot 2LiBO_2$ has a triangular shape ("becomes wedge-shaped") and ends in a point of double rise ("transition" point).

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NEW CASES FOR THE ISOMERIZATION OF COBALT DIOXIMINES

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It was shown by one of us [1] that the phenomenon of coordination polymerism is widely represented for the complexes of trivalent cobalt with dimethylglyoxime, for example:

$$[CoNH_3(DH)_2NO_2] \quad \text{and} \quad [Co(NH_3)_2(DH)_2][Co(DH)_2(NO_2)_2].$$

Also introduced in the nature of the acid radical were Cl and Br; and instead of NH_3, aniline and its derivatives.

It was of interest to obtain salts of type

$$[Co\ Amine_2(DH)_2][Co(DH)_2(NCS)_2] \quad \text{(I) and}$$

to compare them with the nonelectrolytes of type [Co Amine $(DH)_2$ NCS] (II).

Recently we had obtained the compound dithiocyanatobis-(dimethylglyoxime) cobaltic acid $H[Co(DH)_2(NCS)_2]$, which gives well-crystallized salt with different metals, for example Cu, Cd, Zn, etc. [2]. When solutions of the dithiocyanato acid and salts of type $[Co\ Amine_2(DH)_2]Cl$ (where Amine = NH_3 or organic amine) are mixed, there deposit, in accord with the reaction

$$[Co\ Amine_2(DH)_2]X + H[Co(DH)_2(NCS)_2] = [Co\ Amine_2(DH)_2][Co(DH)_2(NCS)_2] + HX$$

crystalline precipitates, difficultly soluble in water. In addition to their mode of synthesis, the reaction of these compounds with acids also serves as proof of their structure. Actually, when the substances are treated with hydrochloric acid, the dithiocyanatobis (dimethylglyoxime) cobaltic acid is obtained in nearly quantitative yield.

Of the compounds of type [Co Amine $(DH)_2$ NCS] the compounds [CoPy $(DH)_2$ NCS] [3] and $[CoNH_2C_6H_5(DH)_2NCS]$ [4], have been described in the literature.

Other compounds of this type were synthesized by us, where the amines taken by us were ammonia and nuclear-substituted aniline derivatives. The compound $[CoNH_3(DH)_2NCS]$ was obtained by the air-oxidation of a mixture of cobalt acetate, dimethylglyoxime and ammonium thiocyanate.

The salt-nonelectrolytes of type [Co Amine $(DH)_2$ NCS] were prepared by the Chugaev method [5]. As experiment revealed, the order of adding the components possesses very great significance. To obtain the nonelectrolyte in pure form the dimethylglyoxime (2 moles) in admixture with the amine (2 moles) was dissolved in alcohol, and then the cobalt salt (1 mole) and ammonium thiocyanate were added to the solution. The mixture was oxidized by passing air through it. The nonelectrolyte is formed in accord with the reaction:

$$2Co(NO_3)_2 + 4DH_2 + 2NH_4SCN + 2\ Amine + 1/2\ O_2 = 2[Co\ Amine\ (DH)_2NCS] + 2NH_4NO_3 + 2HNO_3 + H_2O$$

and is obtained as a crystalline precipitate. With the indicated sequence of adding the components the insoluble cobalt salt of the dithiocyanatobis (dimethylglyoxime) cobaltic acid, which can contaminate the product, fails

to be formed. In some cases the nonelectrolyte separates from the reaction mixture only after the addition of a small amount of water. All of the substances obtained by us are difficultly soluble in water, and consequently it was impossible to determine their electrical conductivity. However, their method of preparation leaves no doubt as to their being nonelectrolytes. The chemical behavior of our compounds differs from that of the complex salts [Co Amine $_2$(DH)$_2$] [Co(DH)$_2$(NCS)$_2$]: they are not changed by hydrochloric acid.

Among the salt-nonelectrolytes obtained by us there exist two compounds – [Co(o–$NH_2C_6H_4CH_3$)(DH)$_2$ NCS] and [Co (p-$NH_2C_6H_4CH_3$)(DH)$_2$NCS], which show isomerism, conditioned by the different position of substituents in the benzene ring [1].

Some of the complex salts (I) obtained by us are coordination dimers of the salt-nonelectrolytes (II).

(II)	(I)
[$CoNH_2C_6H_5$(DH)$_2$NCS]	[Co($NH_2C_6H_5$)$_2$(DH)$_2$][Co(DH)$_2$(NCS)$_2$]
[Co(p-$NH_2C_6H_4CH_3$)(DH)$_2$NCS]	[Co(o-$NH_2C_6H_4CH_3$)$_2$(DH)$_2$][Co(DH)$_2$(NCS)$_2$]
[Co(p-$NH_2C_6H_4OCH_3$)(DH)$_2$NCS]	[Co(p-$NH_2C_6H_4OCH_3$)$_2$(DH)$_2$][Co(DH)$_2$(NCS)$_2$]
[CoPy(DH)$_2$NCS]	[CoPy$_2$(DH)$_2$][Co(DH)$_2$(NCS)$_2$].

EXPERIMENTAL

1. Bis (dimethylglyoxime) diamminecobalt Dithiocyanato-bis (dimethylglyoxime) cobaltate

To obtain [Co(NH_3)$_2$(DH)$_2$][Co(DH)$_2$(NCS)$_2$] 1 g of the dithiocyanato acid H[Co(DH)$_2$(NCS)$_2$] was dissolved with slight warming in 60 ml of water. To the filtered solution was added a solution of 1 g of bis (dimethylglyoxime) diaminecobalt thiocyanate, [Co(NH_3)$_2$(DH)$_2$] SCN · H_2O, in 30 ml of water; here some handsome golden-brown crystals were obtained as scales. The precipitate was filtered, washed with alcohol, and air-dried. Under the microscope the substance appears as thin light-yellow rectangular plates. Yield ~85%. Insoluble in water and alcohol.

Analysis of the Air-Dried Substance

Found %: Co 16.10; SCN 16.06; S 8.94.

[Co($C_4H_{10}O_2N_3$)$_2$] [Co($C_4H_7N_2O_2$)$_2$(NCS)$_2$]. Calculated %: Co 16.18; SCN 15.95; S 8.81.

To prove that the compound is actually bis(dimethylglyoxime) - diaminecobalt dithiocyanatobis (dimethylglyoxime) cobaltate the substance was covered with dilute hydrochloric acid (1:1), where the glistening scale crystals were transformed into a finely crystalline reddish-brown product.

Qualitative tests with Co^{2+}, Cu^{2+} and Cd^{2+} ions revealed that the dithiocyanato acid had been formed. The conversion of the complex salt into the dithiocyanato acid is quantitative:

0.4273 g. [Co(NH_3)$_2$(DH)$_2$][Co(DH)$_2$(NCS)$_2$] gave 0.2278 g. H[Co(DH)$_2$(NCS)$_2$]; theory should be 0.2388.

2. Bis(dimethylglyoxime) (dianiline) cobalt Dithiocyanato-bis (dimethylglyoxime) cobaltate

To obtain the [Co($NH_2C_6H_5$)$_2$(DH)$_2$][Co(DH)$_2$(NCS)$_2$] and other compounds, an equivalent amount of bis(dimethylglyoxime) (dianiline) cobalt thiocyanate, dissolved in a mixture of water and alcohol under slight warming, was added to a filtered aqueous solution of the dithiocyanato acid. Cooling of the mixture gave fine yellow-brown lustrous scale crystals. Under the microscope the compound appears as light-yellow, thin, regularly-shaped rectangular plates. Insoluble in water and alcohol.

Analysis of the Air-Dried Substance

Found %: Co 13.27, 13.29; SCN 13.36, 13.41.

[Co(C_6H_7N)$_2$($C_4H_7N_2O_2$)$_2$][Co($C_4H_7N_2O_2$)$_2$(NCS)$_2$]. Calculated %: Co 13.39; SCN 13.19.

3. Bis(dimethylglyoxime) di (o-toluidine) cobalt Dithiocyanato-bis (dimethylglyoxime) cobaltate

[Co(o-$NH_2C_6H_4CH_3$)$_2$(DH)$_2$][Co(DH)$_2$(NCS)$_2$] fine brownish-yellow crystals. Under the microscope the compound appears as long yellow rods (yield ~60%).

Found %: Co 13.14, 13.16; SCN 12.75; S 6.88.
$[Co(C_7H_9N)_2(C_4H_7N_2O_2)_2][Co(C_4H_7N_2O_2)_2(NCS)_2]$. Calculated %: Co 12.97; SCN 12.78; S 7.04.

4. Bis(dimethylglyoxime) di (p-toluidine) cobalt Dithiocyanatobis (dimethylglyoxime)-cobaltate

$[Co(p\text{-}NH_2C_6H_4CH_3)_2(DH)_2][Co(DH)_2(NCS)_2] \cdot H_2O$ – golden brown crystals. Under the microscope the compound appears as thin yellow-orange rectangular plates. Dissolves with difficulty in water and alcohol.

Found %: Co 12.77; SCN 12.51; S 6.56; H_2O 1.91, 1.90. $[Co(C_7H_9N)_2(C_4H_7N_2O_2)_2]$ $[Co(C_4H_7N_2O_2)_2(NCS)_2] \cdot H_2O$. Calculated %: Co 12.72; SCN 12.54; S 6.92.

Analysis of the Substance Dried at 105°

Found %: Co 13.00. $[Co(C_7H_9N)_2(C_4H_7N_2O_2)_2][Co(C_4H_7N_2O_2)_2(NCS)_2]$. Calculated %: Co 12.97.

5. Bis(dimethylglyoxime) di (p-anisidine) cobalt Dithiocyanato bis (dimethylglyoxime) cobaltate

$[Co(p\text{-}NH_2C_6H_4OCH_3)_2(DH)_2][Co(DH)_2(NCS)_2]$ – fine red-brown crystals. Under the microscope appears as yellow-brown rods. Yield 70%.

Found %: Co 12.54, 12.53; SCN 12.64, 12.53; S 6.48. $[Co(C_7H_9ON)_2(C_4H_7N_2O_2)_2][Co(C_4H_7N_2O_2)_2(NCS)_2]$. Calculated %: Co 12.53; SCN 12.35; S 6.81.

6. Bis(dimethylglyoxime) di (p-chloroaniline) cobalt Dithiocyanatobis (dimethylglyoxime) cobaltate

$[Co(p\text{-}NH_2C_6H_4Cl)_2(DH)_2][Co(DH)_2(NCS)_2] \cdot H_2O$ – dark yellow crystalline powder. Under the microscope appears as yellow plates. Yield 70%. When heated to 105-110° the substance loses water. In the air, gradually attracting moisture, the compound acquired 1 mole of water.

Found %: Co 12.21, 12;31; SCN 12.01, 12.12; H_2O 1.89, 1.69. $[Co(C_6H_6NCl)_2(C_6H_7N_2O_2)_2]$ $[Co(C_4H_7N_2O_2)_2(NCS)_2] \cdot H_2O$. Calculated %: Co 12.18; SCN 12.00; H_2O 1.86.

Analysis of the Substance Dried at 105°

Found %: Co 12.51. $[Co(C_6H_6NCl)_2(C_4H_7N_2O_2)_2][Co(C_4H_7N_2O_2)_2(NCS)_2]$. Calculated %: Co 12.42.

This substance was investigated in the same manner as the first compound: when covered with dilute hydrochloric acid (1:1) the dithiocyanato acid is formed:

0.4536 g. $[Co(p\text{-}NH_2C_6H_4Cl)_2(DH)_2][Co(DH)_2(NCS)_2] \cdot H_2O$ gave 0.3780 g. $H[Co(DH)_2(NCS)_2]$; theory requires 0.3811 g.

7. Bis(dimethylglyoxime) di (p-bromoaniline) cobalt Dithiocyanatobis (dimethylglyoxime) cobaltate

$[Co(p\text{-}NH_2C_6H_4Br)_2(DH)_2][Co(DH)_2(NCS)_2] \cdot H_2O$ – dark red-brown crystalline powder. Under the microscope appears as long brownish-yellow rectangular rods.

Found %: Co 11.24, 11.24; SCN 11.19; H_2O 1.44, 1.54. $[Co(C_6H_6NBr)_2(C_4H_7N_2O_2)_2][Co(C_4H_7N_2O_2)_2(NCS)_2] \cdot H_2O$. Calculated %: Co 11.15; SCN 10.99; H_2O 1.70.

8. Bis(dimethylglyoxime) di (p-iodoaniline) cobalt Dithiocyanatobis (dimethylglyoxime) cobaltate

$[Co(p\text{-}NH_2C_6H_4I)_2(DH)_2][Co(DH)_2(NCS)_2]$ – golden-brown scales. Under the microscope appears as fine thin yellow plates.

Found %: Co 10.37, 10.48; SCN 9.91; S 5.70. $[Co(C_6H_6NI)_2(C_4H_7N_2O_2)_2][Co(C_4H_7N_2O_2)_2(NCS)_2]$. Calculated %: Co 10.41; SCN 10.26; S 5.66.

9. Bis(dimethylglyoxime) di (m-nitroaniline) cobalt Dithiocyanatobis (dimethylglyoxime) cobaltate

$[Co(m\text{-}NH_2C_6H_4NO_2)_2(DH)_2][Co(DH)_2(NCS)_2] \cdot H_2O$ – brown crystalline powder. Under the microscope appears as star-shaped clumps of fine rods.

Found %: Co 12.19, 12.13; SCN 11.91; H_2O 1.59. $[Co(C_6H_6O_2N_2)_2(C_4H_7N_2O_2)_2][Co(C_4H_7N_2O_2)_2(NCS)_2]$. Calculated %: Co 11.92; SCN 11.75; H_2O 1.82.

10. Bis(dimethylglyoxime) dipyridinecobalt Dithiocyanatobis (dimethylglyoxime) cobaltate

$[CoPy_2(DH)_2][Co(DH)_2(NCS)_2]$ – grayish-yellow crystalline powder. Under the microscope appears as

thin yellow plates.

Found %: Co 13.66, 13.74; SCN 13.87, 13.83. $[Co(C_5H_5N)_2(C_4H_7N_2O_2)_2][Co(C_4H_7N_2O_2)_2(NCS)_2]$. Calculated %: Co 13.82; SCN 13.62.

11. Thiocyanatobis (dimethylglyoxime) amminecobalt

The salt-nonelectrolytes of composition [Co Amine $(DH)_2$ NCS] were obtained by the general method of L. A. Chugaev [3]. A solution of 2.3 g. of dimethylglyoxime in 50 ml of alcohol was prepared by heating under reflux. To this solution was added a mixture of 2.5 g of $Co(CH_3COO)_2 \cdot 4H_2O$ and 0.7 g NH_4SCN in 20 ml of H_2O. The passage of air through the solution gradually gave a finely crystalline light-brown precipitate. The precipitate was washed with hot water, and then with alcohol. Yield ~ 80 %.

Analysis of the Air-Dried Substance

Found %: Co 15.72, 15.73; SCN 15.24, 1528; H_2O 2.35, 2.20; N 23.22, 22.79. $[CoNH_3(C_4H_7N_2O_2)_2NCS] \cdot 1/2\ H_2O$. Calculated %: Co 15.79; SCN 15.56; H_2O 2.41; N 22.52.

12. Thiocyanatobis (dimethylglyoxime) (o-toluidine) cobalt

To obtain $[Co(o\text{-}NH_2C_6H_4CH_3)(DH)_2NCS]$ a mixture of 2.3 g of dimethylglyoxime and 2.0 g of o-toluidine was dissolved under heating in 50 ml of alcohol. To the filtered and still warm solution was added 2.9 g of cobalt nitrate and 1.5 g of ammonium thiocyanate in 30 ml of water. When air was passed through the solution a finely crystalline red-brown precipitate was gradually formed. Yellow rhombic crystals under the microscope. The precipitate was washed with hot water, and then with alcohol.

Analysis of the Air-Dried Substance

Found %: Co 12.81, 12.74; SCN 12.81; N 18.67. $[Co(C_7H_9N)(C_4H_7N_2O_2)_2NCS]$. Calculated %: Co 12.97; SCN 12.78; N 18.49.

13. Thiocyanatobis (dimethylglyoxime) (p-toluidine) cobalt

$[Co(p\text{-}NH_2C_6H_4CH_3)(DH)_2NCS]$ was obtained in the same manner as the preceding compound. Brown powder. Yellow plates under the microscope.

Found %: Co 12.94, 13.01; SCN 12.78. $[Co(C_7H_9N)(C_4H_7N_2O_2)_2NCS]$. Calculated %: Co 12.97; SCN 12.78.

14. Thiocyanatobis (dimethylglyoxime) (p-anisidine) cobalt

$[Co(p\text{-}NH_2C_6H_4OCH_3)(DH)_2NCS]$ – dark brown crystalline powder. Orange-brown rhombs under the microscope.

Found %: Co 12.43, 12.44; SCN 12.41, 12.35. $[Co(C_7H_9ON)(C_4H_7N_2O_2)_2NCS]$. Calculated %: Co 12.53; SCN 12.35.

15. Thiocyanatobis (dimethylglyoxime) (p-chloroaniline) cobalt

$[Co(p\text{-}NH_2C_6H_4Cl)(DH)_2NCS]$ – fine lustrous dark brown microscopic plates. The substance is readily soluble in alcohol and can be recrystallized from it.

Found %: Co 12.40, 12.36; SCN 12.37, 12.32. $[Co(C_6H_6NCl)(C_4H_7N_2O_2)_2NCS]$. Calculated %: Co 12.42; SCN 12.23.

The substance was covered with dilute hydrochloric acid (1:1), where it remained without change. The obtained product was analyzed.

Found %: SCN 12.06. $[Co(C_6H_6NCl)(C_4H_7N_2O_2)_2NCS]$. Calculated %: SCN 12.23.

16. Thiocyanatobis (dimethylglyoxime) (p-bromoaniline) cobalt

The preparation of $[Co(p\text{-}NH_2C_6H_4Br)(DH)_2NCS] \cdot H_2O$ was associated with some difficulties. It is best obtained in the following manner: the dark brown alcohol solution, obtained after passing air through it, is filtered and then water is added to it with care. Light-brown crystals are obtained.

Found %: Co 10.77, 11.07, 11.04, 10.78; SCN 11.08; H_2O 3.92, 3.85. $[Co(C_6H_6NBr)(C_4H_7N_2O_2)NCS] \cdot H_2O$. Calculated %: Co 10.97; SCN 10.81; H_2O 3.35.

17. Thiocyanatobis(dimethylglyoxime)(p-iodoaniline) cobalt

$[Co(p\text{-}NH_2C_6H_4I)(DH)_2NCS] \cdot 2H_2O$ – brown-yellow microscopic prisms. Readily soluble in alcohol.

Found %: Co 9.96, 9.67; SCN 9.67, 9.58; S 5.59; H_2O 5.86, 6.34. $[Co(C_6H_6NI)(C_4H_7O_2N_2)_2NCS] \cdot 2H_2O$. Calculated %: Co 9.79; SCN 9.65; S 5.32; H_2O 5.98.

18. Thiocyanatobis(dimethylglyoxime)(m-nitroaniline) cobalt

$[Co(m\text{-}NH_2C_6H_4NO_2)(DH)_2NCS]$ – fine red-brown crystals. Yellow triangular prisms under the microscope. Insoluble in water and alcohol.

Found %: Co 12.04, 12.05; SCN 11.69; S 6.92. $[Co(C_6H_6O_2N_2)(C_4H_7N_2O_2)_2NCS]$. Calculated %: Co 12.15; SCN 11.97; S 6.61.

SUMMARY

1. The salt-nonelectrolytes of type $[Co\ Amine\ (DH)_2NCS]$ (II), were obtained, where Amine = ammonia, o-toluidine, p-toluidine, p-anisidine, p-chloroaniline, p-bromoaniline, p-iodoaniline and m-nitroaniline.

2. The compounds $[Co(o\text{-}NH_2C_6H_4CH_3)(DH)_2NCS]$ and $[Co(p\text{-}NH_2C_6H_4CH_3)(DH)_2NCS]$ appear as isomers with respect to the position of the substituents in the benzene ring.

3. Proceeding from dithiocyanatobis (dimethylglyoxime) cobaltic acid the salts of type $[Co(Amine)_2(DH)_2][Co(DH)_2(NCS)_2] \cdot xH_2O$ (I), were obtained, where Amine = ammonia, aniline, o-toluidine, p-toluidine, p-anisidine, p-chloroaniline, p-bromoaniline, p-iodoaniline, m-nitroaniline and pyridine.

4. Some of the complex salts of type (I) appear as dimers of the salt-nonelectrolytes of type (II).

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THE MOLECULAR WEIGHT OF SOME TITANIUM TETRACHLORIDE COMPLEXES

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The present work is a continuation of the physicochemical study of the interrelationships existing between the esters of monobasic acids and titanium tetrachloride. Earlier it was shown that titanium tetrachloride with the esters of monobasic acids forms in the liquid phase complexes of predominant composition 1:1, and not with two moles of ester, as is the case for tin tetrachloride [1-4].

The purpose of the present work was to establish the molecular composition of the complexes, formed by $TiCl_4$ with the isobutyl and isoamyl esters of butyric acid and the ethyl ester of chloroacetic acid.

To establish the composition of the complexes we used the methods of physicochemical analysis, and specifically we studied the viscosity, electrical conductivity, liquefaction and density of the systems: $TiCl_4$–$C_3H_7COOC_4H_9$, $TiCl_4$–$C_3H_7COOC_5H_{11}$ and $TiCl_4$–$CH_2ClCOOC_2H_5$.

The results of studying the indicated properties for our systems as a function of composition revealed that $TiCl_4$ with the indicated esters forms thermally stable complexes of composition 1:1; as a result, in studying the molecular weights of the complexes we proceeded from equimolar ratios of the components.

Method of Operation and Materials. The cryoscopic determinations were run in an apparatus having good air-tightness, since the presence of even traces of moisture in the solution of the complex can lead to appreciable errors, due to hydrolysis of the titanium tetrachloride. Hot dry air was blown through the apparatus prior to each determination. All of the substances, taken for the work, were kept in sealed ampuls.

We took benzene (K = 5.12) as the solvent for the molecular weight determinations.

The benzene of "cryoscopic" grade was allowed to stand over metallic mercury for several days to remove traces of sulfur compounds. Then it was dried over metallic sodium, from which it was also distilled. For the work the fraction with b. p. 79.9–80.1° (760 mm) was collected n_D^{20} 1.5013, d_4^{20} 0.8791.

The titanium tetrachloride was synthesized in known manner [5]. The obtained product was kept for several days over metallic mercury and then was distilled from it through a peculiar (special) purifier, filled 1/5 with mercury. The titanium tetrachloride purified in this manner had b. p. 136.4° (760 mm), d_4^{20} 1.7273.

The ethyl ester of chloroacetic acid and the isobutyl and isoamyl esters of butyric acid were dried for a long time over freshly ignited calcium chloride, and then were fractionally distilled. For the work the fractions boiling in the following limits were collected: $CH_2ClCOOC_2H_5$ 144–144.2°, $C_3H_7COOC_4H_9$ 156.6–157.0°, $C_3H_7COOC_5H_{11}$ 178.3–178.8°.

The Cryoscopic Study Results are given in Tables 1 - 3.

Molecular weight of $TiCl_4 \cdot C_3H_7COOC_4H_9$ $M_{theor.}$ = 333.94.

The presented data testify to the fact that at low concentrations of the order of 0.2–0.4 mole % the molecules of the complexes $TiCl_4 \cdot C_3H_7COOC_4H_9$ and $TiCl_4 \cdot C_3H_7COOC_5H_{11}$ are found in the form of

monomers. For the compound $TiCl_4 \cdot CH_2ClCOOC_2H_5$ such a situation arises at higher concentrations, and specifically at a content of 0.6–0.7 mole % of the complex in solution. With increase in the concentration of the complex the degree of association

$$\frac{M_{exptl.}}{M_{theor.}}$$

increases, reaching 15–20% at concentrations of 3-4 mole %.

TABLE 1

Molal fractions of the complex	$\Delta t°$	Mexptl.	$\frac{M_{exptl.}}{M_{theor.}}$
0.0384	2.220	404	1.21
0.0224	1.530	391	1.17
0.0133	0.902	381	1.14
0.0083	0.561	372	1.11
0.0053	0.257	366	1.09
0.0036	0.225	345	1.03
0.0026	0.201	331	1.00

TABLE 2

Molecular Weight

$TiCl_4 \cdot C_3H_7COOC_6H_{11}$ ($M_{theor.}$ = 347.96)

Molal fractions of the complex	$\Delta t°$	$M_{exptl.}$	$\frac{M_{exptl.}}{M_{theor.}}$
0.0370	1.940	401	1.15
0.0241	1.201	397	1.14
0.0150	0.739	395	1.13
0.0092	0.440	385	1.10
0.0054	0.265	381	1.09
0.0042	0.172	350	1.00

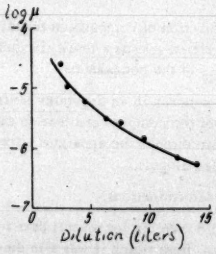

TABLE 3

Molecular Weight

$TiCl_4 \cdot CH_2ClCOOC_2H_5$ ($M_{theor.}$ = 312.25)

Molal fractions of the complex	$\Delta t°$	$M_{exptl.}$	$\frac{M_{exptl.}}{M_{theor.}}$
0.0320	1.550	371	1.19
0.0172	0.891	333	1.07
0.0095	0.501	321	1.03
0.0067	0.379	309	1.00

It should be mentioned that the values given by us for the molecular weights of the complexes in benzene are to a certain degree an average value, for the solutions possess considerable electrical conductivity, which suggests that products capable of conducting a current are present, which products are obtained as the result of the electrolytic dissociation of the complex.

Investigation of the Specific Electrical Conductivity of the Compound $TiCl_4 \cdot C_3H_7COOC_4H_9$ in benzene at 20° revealed that with concentration increase for the complex its conductivity increases, as can be seen from the Figure, where along the ordinate axis the logarithms of the molecular electrical conductivity values are plotted, while along the abscissa the dilution is plotted (in liters).

As a result, an increase in the degree of association with concentration increase for the complex also accounts for the simultaneous increase in the electrical conductivity. There exist a number of indications in the literature for such parallel increase in both molecular weight and electrical conductivity with increase in the amount of complex in solution [6-8].

Z. A. Yankelevich and I. A. Sheka associate this phenomenon with the presence of electrolytic dissociation for the associated molecules of the complex compound.

As is evident from our data, in the region of our investigated concentration, the degree of association is found to range from 1 to 2, consequently, it can be assumed that for complexes there exists in solution the equilibrium: $[2TiCl_4 \cdot E]_2 \rightleftarrows [TiCl_4 \cdot E]_2$, (where E is the corresponding ester molecule), which at very high dilutions is strongly shifted to the left, i. e. in the direction of monomer formation.

Since the source of the current-conducting products in the solution are the associated molecules of the complex, then, consequently, on increasing the concentration of the latter the electrical conductivity should rise, which fact is supported by the data shown in the Figure.

Proceeding from the presence of association for the complex compound and the rise in its conductivity with concentration increase, the electrolytic dissociation scheme can be depicted in the following manner:

$$[TiCl_4 \cdot E]_2 \rightleftarrows [TiCl_6]^{--} + [TiCl_2 \cdot 2E]^{++}.$$

The complex cation $[TiCl \cdot 2E]^{++}$ should possess a certain polarizing ability, for which reason it can add to itself another ester molecule and give a cation of type $[TiCl_2 \cdot 4E]^{++}$. Between the indicated two types of complex cations there should also exist the equilibrium condition:

$$[TiCl_2 \cdot 2E]^{++} + 2E \rightleftarrows [TiCl_2 \cdot 4E]^{++}.$$

Consequently, in the reaction of titanium tetrachloride with esters of monobasic acids, together with the presence of complexes having a 1:1 composition, there can also be formed complexes having a 1:2 composition.

Actually, as was shown in our studies [3,4], in some systems, together with complexes of type $TiCl_4 \cdot E$ there also exist complexes of type $TiCl_4 \cdot 2E$ which thermally are less stable than the first. The scheme for the electrolytic dissociation of complexes of type $TiCl_4 \cdot 2E$ can be depicted in the following manner:

$$[TiCl_4 \cdot 2E]_2 \rightleftarrows [TiCl_6]^{--} + [TiCl_2 \cdot 4E]^{++}.$$

There are statements in the literature that the complexes of tin tetrachloride with the esters of monobasic acids dissociate into current-conductive products by a scheme that is analogous to the last one given above [9].

SUMMARY

1. The cryoscopic study of the molecular weights of the compounds: $TiCl_4 \cdot C_3H_7COOC_4H_9$, $TiCl_4 \cdot C_3H_7COOC_5H_{11}$ and $TiCl_4 \cdot CH_2ClCOOC_2H_5$, shows that at low concentrations for these complexes the found molecular weights lie close to the calculated theory. With concentration increase for the complexes the degree of association rises.

2. On the example of the complex, $TiCl \cdot C_3H_7COOC_4H_9$, it was shown that the rise in the degree of association with increase in concentration is also accompanied by an increase in the electrical conductivity; consequently, the source of the current-conductive products in the solution are the associated complexes.

3. On the basis of the obtained data, schemes have been presented for the electrolytic dissociation of complexes of type $TiCl \cdot E$ and $TiCl_4 \cdot 2E$.

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Rostov-on-Don State University

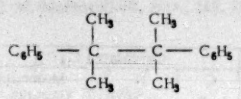
* T.p. = C. B. translation pagination.

MECHANISM OF THE GRIGNARD-WURTZ REACTION

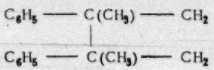
II. SYNTHESIS AND PROPERTIES OF 2, 3-DIPHENYL-2,3-DIMETHYLBUTANE

A. A. Yavorovsky and M. S. Malinovsky

The hydrocarbon $C_{18}H_{22}$, corresponding to 2,3-diphenyl-2,3-dimethylbutane (I), was first obtained by Wallach in 1899 from the amide of phenylisobutyric acid [1]. In 1902 Klages [2] synthesized a hydrocarbon of the same structure by the reduction of iodoisopropylbenzene. However, since Klages' hydrocarbon differed sharply in its melting point (119-120°) from Wallach's hydrocarbon (m. p. 55-56°), Klages proposed a different formula (I)* for his compound, although the method of preparation clearly indicated formula (I):



(I)



(II)

In 1949 I. Lapkin and A. Lyubimova [3] isolated a hydrocarbon with m. p. 118°, to which, on the basis of its method of preparation, they assigned formula (I), further stating that this hydrocarbon was previously unknown. In a footnote Lapkin and Lyubimova point to the error of Wallach's conclusions relative to the structure of his hydrocarbon, however, they fail to mention Klages' work.

We repeated the synthesis of Lapkin and Lyubimova, proceeding from the pure α-bromo-α-methyl ethylbenzene [4], and reacting the latter in ether solution with magnesium. The hydrocarbon $C_{18}H_{22}$ with m. p. 119-120° was obtained as a result, which on the basis of its method of preparation corresponds to formula (I). Together with the indicated solid hydrocarbon, a liquid hydrocarbon with a formula close to $C_{18}H_{22}$ was also obtained. Some formation of the latter was also always observed even when the solid hydrocarbon was subjected to high-vacuum distillation.

We also obtained 2,3-diphenyl-2,3-dimethylbutane by the Wurtz reaction from α-bromo-α-methylethyl-benzene. In this case also, in addition to the solid hydrocarbon with m. p. 119-120°, the liquid hydrocarbon was obtained, and here in considerably greater amount than in the previous experiment. It was postulated by us that the liquid hydrocarbon is formed as the result of partial isomerization of the solid 2,3-diphenyl-2,3-dimethylbutane. To confirm this postulation we heated the hydrocarbon having m. p. 119-120° with an iodine crystal in a sealed tube. Here the liquid hydrocarbon was obtained in 73.5 % yield as a colorless liquid with aromatic odor, distilling completely from metallic sodium at 150-151° (745 mm) and at 36-36.5° (8 mm). In addition to the liquid hydrocarbon, a small amount of a solid substance with m.p. 206-206.5° was found in the ampul, in its elementary composition corresponding to the hydrocarbon $C_{18}H_{22}$. All three hydrocarbons, the two with m. p. 119-120° and 206-206.5° and the liquid hydrocarbon, gave acetophenone when oxidized. For the hydrocarbons with m. p. 119-120° and 206-206.5° the x-ray patterns were taken by the powder method, in which patterns the character of the lines and their distribution proved to be the same, but the distances between them were different. This suggests different crystal lattice parameters.

* Formula I in original is evidently in error. Should say Formula II. – Publisher.

We also repeated the synthesis of the hydrocarbon $C_{18}H_{22}$ by the Wallach method. Here we obtained a small amount of substance with m. p. 52-53°, which is somewhat lower than the melting point given by Wallach for his hydrocarbon. Analysis of the hydrocarbon supported the formula $C_{18}H_{22}$.

EXPERIMENTAL

In a three-necked flask, fitted with a mercury-seal stirrer, condenser with calcium chloride tube, thermometer, and dropping funnel, was placed 6 g of magnesium, 15 ml of ether and about 1 ml of α-bromo-α-methylethylbenzene. The mixture was boiled for 10 minutes and then under gentle ether boil was added over 1 hour a solution of 48.5 g of the bromide in 140 ml of ether. The mixture was boiled for another hour, cooled, and treated with water. From the ether solution 29 g of liquid was isolated, which congealed on standing. After pressing on porous plate there was obtained 10 g of crystals with m. p. 119-120° (from ethyl alcohol) and b. p. 90-91° (0.001 mm). The analysis of this hydrocarbon is given in the Table.

The porous plate, on which the crystals had been pressed, was broken up and then extracted with ether in the Soxhlet apparatus. The ether extract yielded 15 g of liquid, which was vacuum-distilled: First fraction with b. p. 45-47° (10 mm), 5 g; second fraction with b. p. 144-146° (5 mm), 6 g; residue in flask, 3 g.

The first fraction was methylstyrene. The second fraction was crystalline 2, 3-diphenyl-2, 3-diphenyl-2, 3-dimethylbutane (m. p. 119-120°) with a considerable amount of a liquid hydrocarbon.

TABLE

Hydrocarbon Analyses

Expt. Nos.	Melting Point	Boiling Point	Found			Calculated $C_{18}H_{22}$		
			C in %	H in %	Molecular Weight	C in %	H in %	Molecular Weight
1	119—120°	90—91° (0.001 mm)	90.91	9.27	233.6	90.79	9.21	238
2	206—206.5	—	91.18	9.31	228	90.79	9.21	238
3	—	150—151 * (745 mm)	91.49	9.19	—	90.79	9.27	—
4	52—53	—	91.50	9.39	245	90.79	9.21	238

* n^{20} 1.494, d^{20} 0.864

For the Wurtz synthesis there was taken 25 g of α-bromo-α-methylethylbenzene, 5 g of sodium wire and 60 g of ether. The mixture was boiled for 4 hours, after which it was allowed to stand for 24 hours. After the usual treatment there was obtained 12 g of liquid that failed to crystallize, from which after a week there deposited a single crystal with m. p. 118° (from alcohol).

The 2, 3-diphenyl-2, 3-dimethylbutane (15 g) was isomerized under the conditions of heating with an iodine crystal in a sealed tube at 235-240° for 8 hours. Here a brown mobile liquid was obtained and 1 g of crystals with m. p. 206-206.5° (from acetone). The mobile liquid with an aromatic odor distilled completely from metallic sodium at 150-151° (745 mm). The analyses of the liquid and of the crystalline substance are given in the Table.

The oxidation of the hydrocarbons with m. p. 119-120° and 206-206.5° respectively, and of the liquid hydrocarbon with b. p. 150-151°, by boiling for 5 hours with alkaline potassium permanganate solution, in all cases gave acetophenone, which was identified as the semicarbazone with m. p. 192-193°, which semicarbazone failed to show a melting point depression when mixed with authentic acetophenone semicarbazone.

The hydrocarbon $C_{18}H_{22}$, described by Wallach, was obtained from 3.5 g of phenylisobutyramide [1-5]. A small amount of crystals with m. p. 52-53° (from alcohol) was obtained, the analysis of which is given in the Table.

SUMMARY

1. The hydrocarbons, synthesized by Klages and Wallach, have the general formula $C_{32}H_{22}$, but differ in physicochemical properties.

2. The heating of Klages' hydrocarbon (with m. p. 119-120°) in an ampul with an iodine crystal gave two hydrocarbons having the same composition as the original hydrocarbon, but one of them is a liquid with b. p. 151-152°, while the second is a solid with m. p. 206-206.5°.

3. The oxidation of the two solid hydrocarbons with m. p. 119-120° and 206-206.5°, respectively, and of the liquid hydrocarbon with b. p. 151-152°, in all cases gave acetophenone, which points to their identical structure. The x-ray patterns also support their identical structure.

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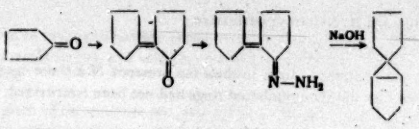
REACTIONS OF HYDRAZINE DERIVATIVES

I. SYNTHESIS OF 1, 1-PENTAMETHYLENEBICYCLO [0, 1, 4] HEPTANE

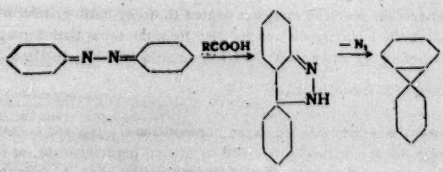
A. N. Kost and I. I. Grandberg

The synthesis of 1, 1-tetramethylenebicyclo [0, 1, 3] hexane by the following scheme was described in one of the papers by N. D. Zelinsky and N. I. Shuikin [1].



The reaction proceeded, apparently, through the intermediate closure of the cyclopentylidenecyclopentanone hydrazone into the pyrazoline base with subsequent nitrogen cleavage. Later, the same authors [2] made an attempt to synthesize 1, 1-pentamethylenebicyclo [0, 1, 4] heptane by this method. But here ring closure of the hydrazone failed to occur, and instead cyclohexylidenecyclohexane was obtained. In the reduction of cyclohexanone azine with formic acid [3] we had to contend with the secondary process of 3, 4-tetramethylene-5, 5-pentamethylenepyrazoline formation, which compound had been described earlier by Stolle [4], but without proof of its structure.

We investigated the conditions for the conversion of cyclohexanone azine into the pyrazoline base, and the cleavage of the latter by the N. M. Kizhner method, and obtained 1, 1-pentamethylenebicyclo [0, 1, 4] heptane in good yield.



The best yields of the pyrazoline base were obtained with oxalic acid (Table 1). Anhydrous formic acid also gave excellent results, but with temperature elevation the pyrazoline suffered partial formylation, while at low temperature 20-30 hours was required for the reaction to be completed. In studying the different alkaline agents for decomposing the pyrazoline the best results were obtained with lithium hydroxide (up to now not used in the Kizhner reaction), which functioned more vigorously than either sodium hydroxide or potassium hydroxide, and gave a small amount of tarry products (Table 2).

The elementary analysis, molecular refraction and parachor of 1, 1-pentamethylenebicyclo [0, 1, 4] heptane agreed well with the calculated values.

TABLE 1

Rearrangement of Cyclohexanone Azine Into the Pyrazoline

Agent	Moles of acid per mole of Azine	Temperature	Time (in hrs.)	Yield of Pyrazoline (in %)	Amount of Starting Azine Recovered (in %)
Anhydrous HOOC – COOH	1.1	70—80°	2	90.6	0
	1.2	100	3	79	0
	1.1 *	25	12	41.6	47.4
85% HCOOH	1.1	105	0.5	0	93.3
Anhydrous HCOOH	1.5	20	20	90	0
	1.7	70—80	1	90 **	0
		25	20		
85% HCOOH	5	110	6	90	0

* In ether solution.

** A mixture of the pyrazoline and its N-formyl derivative.

To prove its structure it was necessary: first, to show the presence of a three-membered ring in the compound and, second, to prove that the six-membered rings had not been isomerized.

TABLE 2

Decomposition of the Pyrazoline Base to 1, 1-Pentamethylenebicyclo [0, 1, 4] heptane. *

Agent	Grams per Mole of Pyrazoline	Time (in hrs.)	Yield of Hydrocarbon (in %)
NaOH . . .	30	5	72
LiOH . . .	4	3	75.1
CH_3ONa .	30	3	57.4 **
CH_3OLi . .	20	5	69 **
KOH . . .	20	5	70

* In all of the experiments the reaction mass was heated to strong boiling under reflux for the indicated length of time, after which the hydrocarbon was distilled from the same flask through a dephlegmator. The obtained substance was thoroughly washed with 50% formic acid and then distilled over sodium.

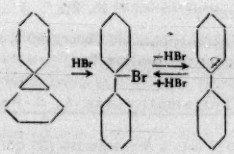
** Considerable tar-formation (resinification).

The obtained hydrocarbon corresponded to the composition $C_{12}H_{20}$ and contained either a double bond, or a three-membered ring, for it was slowly oxidized by neutral permanganate, or rapidly by acid or alkaline permanganate, and it decolorized bromine water. From the studies of N. A. Prilezhaev [5] it is known that a

double bond between two tertiary carbon atoms is instantaneously oxidixed with perbenzoic acid at 0°. This was confirmed by N. D. Zelinsky and N. I. Shuikin [1, 2] on specimens that were very closely similar to ours.

Our hydrocarbon under 5-hour treatment with active perbenzoic acid at 25° was completely recovered with the original constants, which indicates the absence of a double bond in it. An attempt to rupture the three-membered ring with mercury acetate by the P. Ya. Levina and V. N. Kostin method [6] proved unsuccessful. Oxidation was obtained in both alcohol and aqueous solutions, apparently, due to steric hindrance considerations. The smooth rupture of the three-membered ring with bromine also proved unsuccessful, since here together with bromine addition there also proceeded simultaneous substitution, and a complex mixture of substances was obtained. Trauffault [8] showed that the addition of bromine to 1-cyclohexylcyclohexene also proceeds heterogeneously, giving a mixture of addition and substitution products. Then we used the method of opening the three-membered ring with the aid of hydrogen chloride or bromide, in its time a method sucessfully used by N. M. Kizhner for proving the structure of hydrocarbons containing a three-membered ring [7].

The cleavage of hydrogen bromide from the bromide proceeded very easily, in which connection 1-cyclohexylcyclohexene was obtained in quantitative yield:



The repeated addition of hydrogen halides yields substances, completely identical with both the chloride and bromide obtained by Trauffault [8], and with the chloride and bromide obtained by us from 1, 1-pentamethylenebicyclo [0, 1, 4] heptane.

For more complete proof of its structure we used sulfur to dehydrogenate the 1, 1-pentamethylenebicyclo [0, 1, 4] heptane, where we obtained diphenyl (biphenyl). When the 1, 1-pentamethylenebicyclo [0, 1, 4] heptane was subjected to fractional melting all of the fractions had identical constants, which indicates the purity of the substance. The stability of the three-membered ring to reduction proved to be very interesting; it failed to be affected when hydrogenated with platinum black (30 atm., 250°, 4 hours). In the course of our work it was found that the 1, 1-pentamethylenebicyclo [0, 1, 4] heptane could be synthesized without isolating the intermediate reaction products, in which connection the yield reaches 58%, based on cyclohexanone.

EXPERIMENTAL

Preparation of Cyclohexanone Azine. To 196 g (2 moles) of cyclohexanone with vigorous stirring was added 52 g (1 mole) of 96% hydrazine hydrate in 70 ml of water. The addition was made in such manner that the temperature failed to rise above 75-80°. Having added 100 ml of ether, the mixture was allowed to stand for a day.

The whole was transferred to a separatory funnel, 100 ml of water was added, and then 150 ml of ether, after which the top layer was separated and vacuum-distilled. The yield of the azine was 180 g (93.7%).

b. p. 142-146° (10 mm), n_D^{20} 1,5262, m. p. 34°.
Literature: b. p. 175° (28 mm), n_D^{20} 1,5268. m. p. 33-34° [10].

Rearrangement of the Cyclohexanone Azine to the Pyrazoline Base. A. Under very vigorous stirring with a sturdy, power-driven stirrer there was added 49.5 g (0.55 mole) of thoroughly dehydrated powdered oxalic acid to 96 g (0.5 mole) of cyclohexanone azine and the mixture heated at 70-75° for 2 hours in a CO_2 stream. The mixture, solidifying on cooling, was decomposed with a solution of 87 g (0.55 mole) of potash in 600 ml of water and the resulting pyrazoline was extracted with 100 ml of benzene. The benzene extract was vacuum-distilled in a nitrogen stream, or from a flask filled with glass wool.

The yield of the 3, 4-tetramethylene-5, 5-pantamethylenepyrazoline, readily oxidizing in the air, was 87 g, b. p. 165-167° (15 mm) and m. p. 60°.

The phenylcarbamido (phenylureido) derivative had m. p. 122° (from alcohol).

Literature: b. p. 165° (17 mm), m. p. 64°. Phenylureido derivative, m. p. 124° [4].

B. To 38.4 g (0.2 mole) of cyclohexanone azine was added 11.2 g (0.22 mole) of anhydrous formic acid and the mixture was heated on the water bath at 40-50° for 3 hours. The reaction mixture was made alkaline with ammonia and the heavy viscous layer was separated, after which 50 ml of benzene was added to it; the benzene was removed by distillation and the residue was vacuum-distilled.

The yield of 3, 4-tetramethylene-5, 5-pentamethylenepyrazoline was 10.2 g (26.6%), b. p. 162-169° (15 mm), m. p. 60°. The phenylureido derivative had m. p. 121° (from alcohol).

The heavy fraction (28.1 g, b. p. 180-210° at 15 mm) crystallized on prolonged standing. Precipitation with water from alcohol solution gave the N-formyl-3, 4-tetramethylene-5, 5-pentamethylenepyrazoline, m. p. 73°.

Found %: N 12.94. $C_{13}H_{20}N_2O$. Calculated %: N 12.72.

Hydrolysis of this substance with hydrochloric acid (1 hour, 105°), with subsequent alkalization, gave the free base, 3, 4-tetramethylene-5, 5-pentamethylenepyrazoline.

Decomposition of 3, 4-Tetramethylene-5, 5-Pentamethylenepyrazoline

In a 250 ml thick-walled flask, fitted with a dephlegmator (30 cm), was placed 96 g (0.5 mole) of the pyrazoline and 2 g of lithium hydroxide and the mixture heated on a (power-driven) air bath. The formed hydrocarbon was distilled at a rate not exceeding 1 drop in 2-3 seconds (hardly any tar remained in the flask). The hydrocarbon was shaken with 100 ml of 40% formic acid for 2 hours and after this was washed 8 times with 30% formic acid, then once with water, dried over metallic sodium, and finally distilled from sodium. *

The yield of 1, 1-pentamethylenebicyclo [0, 1, 4] heptane was 61.6 g (75.1 %).

b. p. 232-232.5° (746.8 mm), n_D^{20} 1.4973.

After 3-fold distillation from sodium it has the following constants:

b. p. 232° (748 mm), 98° (12 mm) n_D^{20} 1.4972, d_4^{20} 0.9278, MR_D 51.82; Calc. 51.80. Found parachor ** 429.9; Calc. 428.5.

Found %: C 87.57; H 12.42. $C_{12}H_{20}$. Calculated %: C 87.73; H 12.27.

Distillation through a 20-theoretical plate column confirmed the purity of the hydrocarbon. It distilled completely at 98° (12 mm); n_D^{20} 1.4970, d_4^{20} 0.9275.

The 1, 1-pentamethylenebicyclo [0, 1, 4] heptane slowly crystallized when cooled to -73°. By gradually heating and decanting the liquid hydrocarbon we obtained 3 fractions with identical refractive indices, both among themselves and with the original hydrocarbon.

* At times the hydrocarbon on standing turned yellow due to the presence of traces of the pyrazoline, in such case it was washed with 50% formic acid and redistilled.

** The parachor data were obtained by N. I. Stupnikova. The surface tension measurements were made by the method of P. A. Rebinder. The parachor calculations were made according to Sugden.

Synthesis of 1, 1-Pentamethylenebicyclo [0, 1, 4] heptane From Cyclohexanone Without Isolation of the Intermediate Reaction Products

To a flask under a reflux condenser, containing 490 g (5 moles) of cyclohexanone, was added under vigorous stirring over a period of 30 minutes 130 g (2.5 moles) of 96% hydrazine hydrate. After 3-hour heating on the water bath the water was removed by vacuum-distillation until the temperature of the mixture reached 120-130°. The residual azine was placed in a 3-4 liter thick-walled beaker, and stirred very vigorously with a metal stirrer. With the passage of a stream of dry carbon dioxide gas into the beaker there was added 236 g (2.6 moles) of thoroughly ground anhydrous oxalic acid. •

The reaction proceeds with self-heating, the temperature regime was regulated in such manner that for 3 hours it remained in the limits 60-80° under vigorous stirring of the solidifying mixture. After cooling, to the mixture in the beaker was added, with passage of a CO_2 stream, a cold solution of 302 g (about 5.4 moles) of potassium hydroxide in 2 liters of water. After decomposing the pyrazoline oxalate, the whole was placed in a separatory funnel and, having added 100 ml of benzene, the benzene layer was separated. The water layer was extracted once more with 250 ml of benzene. The benzene extracts were placed in a 1 liter thick-walled glass flask and here 1.5 g of lithium hydroxide was added.

The flask was fitted with a wide dephlegmator 30 cm high and the benzene was distilled off. After this the residue was heated either on a power driven air bath or in a sand bath. The formed hydrocarbon was removed by distillation at a rate not exceeding 1 drop in 2 seconds. Further treatment was as in the preceding experiment.

Distillation yielded 231 g of the hydrocarbon (57.8% of the theoretical yield, based on cyclohexanone), b. p. 232° (746.5 mm), n_D^{20} 1.4972, d_4^{20} 0.9277.

Reactions of 1, 1-Pentamethylenebicyclo [0, 1, 4] Heptane Action of Benzoyl Hydroperoxide

The benzoyl hydroperoxide was obtained by the N. A. Prilezhaev method [5]. Ether solutions of equimolecular amounts of the hydrocarbon and fresh active benzoyl hydroperoxide were mixed and the mixture stirred for 5 hours at 25°. After decomposing the hydroperoxide with 10% solium hydroxide solution the hydrocarbon was isolated from the ether extract, which hydrocarbon possessed the original constants and was capable of being oxidized by permanganate. (The activity of the prepared hydroperoxide was first tested on the oxidation of cyclohexane).

Dehydrogenation With Sulfur. A mixture of 16.4 g (0.1 mole) of 1, 1-pentamethylenebicyclo [0, 1, 4] heptane and 16 g (0.5 mole) of powdered sulfur was heated in a flask under reflux for 4 hours at a temperature in the mixture of 190-210°. Steam-distillation from the reaction flask gave 7.0 g (44.5%) of crude diphenyl (biphenyl). After three recrystallizations from 80% alcohol the diphenyl had m. p. 68° and b. p. 254°, which corresponds to the literature data.

Addition of Hydrogen Bromide. Under cooling to 0° a stream of hydrogen bromide was passed for 2 hours into an emulsion composed of 24.6 g (0.15 mole) of 1, 1-pentamethylenebicyclo [0, 1, 4] heptane and 100 ml of glacial acetic acid. The reaction mixture was diluted with 4 parts of water and the heavy 1-bromo-1-cyclohexylcyclohexane was separated. When washed with water the bromide crystallized almost instantly. After drying over sulfuric acid in a vacuum-desiccator in the dark the product had m. p. 39.5°. The yield was quantitative.

The bromide turns dark and develops quite a sharp odor when kept in the air. When heated with

• The acid was dried in a vacuum-oven for 6 hours at 80-90°, ground very thoroughly in a mortar, and then dried another hour in the same oven at 90-100°.

sodium iodide in acetone the bromine fails to be replaced by iodine. The compound easily cleaves hydrogen bromide, even when kept under water, for which reason it cannot be recrystallized.

Crystals with m. p. 44.5° are obtained by freezing from a mixture of methyl alcohol and acetone.

Literature: m. p. 46° [9].

Cleavage of Hydrogen Bromide From 1-Bromo-1-cyclohexylcyclohexane. A mixture of 61.3 g (0.25 mole) of the bromide, 27.9 g (0.3 mole) of aniline and 50 ml of toluene was heated at the boil for 30 minutes on an air bath. The reaction mixture was washed 3 times with 15% sulfuric acid, dried over sodium and then distilled from sodium.

The yield of 1-cyclohexylcyclohexene was 37.1 g (90.5%), b. p. 235-237° (745 mm), n_D^{20} 1.4949.

After another distillation from sodium the 1-cyclohexylcyclohexene has the following unchanging constants: b. p. 236° (745 mm), n_D^{20} 1.4948, d_4^{20} 0.9063, MR_D 52.85; Calc. 52.75.

Literature data: b. p. 237° [9], 238.5° (760 mm) [8], d_4^{20} 0.9010 [9], 0.904 [8]; n_D^{20} 1.4910 [9], 1.493 [8].

Addition of Hydrogen Halides to 1-Cyclohexylcyclohexene. A solution of 1.64 g (0.01 mole) of 1-cyclohexylcyclohexene in 5 ml of glacial acetic acid was saturated with hydrogen chloride, then 20 ml of water was added, and the chloride was suction-filtered.

The yield was quantitative. After recrystallization from methyl alcohol, m. p. 39.5°. The compound failed to depress the melting point when mixed with the chloride obtained from 1, 1-pentamethylenebicyclo [0, 1, 4] heptane.

In the same manner the bromide was obtained in quantitative yield from 16.4 g (0.1 mole) of 1-cyclohexylcyclohexene in 50 ml of glacial acetic acid by treatment with hydrogen bromide at 0°, followed by the addition of 150 ml of water. After freezing from a mixture of acetone and methyl alcohol, m. p. 44.5°. The compound failed to depress the melting point when mixed with the bromide obtained from 1, 1-pentamethylenebicyclo [0, 1, 4] heptane. When hydrogen bromide was cleaved from the compound by heating with aniline the original 1-cyclohexylcyclohexene with b. p. 236° (745.7 mm), n_D^{20} 1.4949, d_4^{20} 0.9063, was obtained.

The heating of a mixture of 16.4 g (0.1 mole) of 1, 1-pentamethylenebicyclo [0, 1, 4] heptane and 50 ml of hydrobromic acid (d 1.4) in a sealed ampul for 2 hours on the water bath failed to open the ring. After washing with water and then distilling there was obtained: 12 g of original hydrocarbon, b. p. 233° (758 mm), n_D^{20} 1.4969.

Addition of Hydrogen Chloride. A stream of hydrogen chloride gas was passed into an emulsion of 16.4 g (0.1 mole) of the investigated hydrocarbon and 50 ml of glacial acetic acid to saturation. After diluting with 4 parts of water the 1-chloro-1-cyclohexylcyclohexane was isolated by suction-filtration, m. p. 38°.

The yield was quantitative. After recrystallization from methyl alcohol, m. p. 39.5°.

Literature: m. p. 40° [9].

Reaction With Mercury Acetate. A mixture of 3.5 g of the hydrocarbon and 50 ml of saturated mercury acetate solution was allowed to stand for 20 days at a temperature of −6 to +5°. The hydrocarbon layer disappeared in this period of time and a white porridgelike precipitate appeared. The reaction mass was evaporated in vacuo to dryness. The residue was extracted with alcohol. The greater portion of the precipitate was soluble in alcohol and was precipitated from it with water. This substance, recrystallized from aqueous alcohol, decomposes when heated to 150-180°; it is soluble in ether, water and hydrocarbons, and readily soluble in alcohols. With two normal alkali or ammonia solution it gives a black precipitate of mercurous mercury. The substance, apparently, is the mercurated oxidation product of the hydrocarbon and contains monovalent mercury. The composition and structure of this substance were not studied in detail. Oxidation also took place under the influence of an alcoholic mercury acetate solution under room temperature conditions for a day.

Hydrogenation of 1, 1-Pentamethylenebicyclo [0, 1, 4] heptane. Into a 250 ml autoclave was charged 32.8 g (0.2 mole) of 1, 1-pentamethylenebicyclo [0, 1, 4] heptane, 50 ml of isooctane and 1.3 g of platinum black, the latter prepared according to Wilstatter. With shaking and a hydrogen pressure of 30 atm. the autoclave was heated for 4 hours at 200-205°. Distillation gave 30.1 g (91.4%) of the original hydrocarbon: b. p. 232° (747.3 mm), n_D^{20} 1.4970, d_4^{20} 0.9274.

SUMMARY

A method was developed for the preparation of 1, 1-pentamethylenebicyclo [0, 1, 4] heptane, the structure of which was proved.

At the same time the structure of 3, 4-tetramethylene-5, 5-pentamethylenepyrazoline was proven, which compound is formed in the rearrangement of cyclohexanone azine.

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REACTIONS OF CHLOROPROPYLENES WITH FORMALDEHYDE

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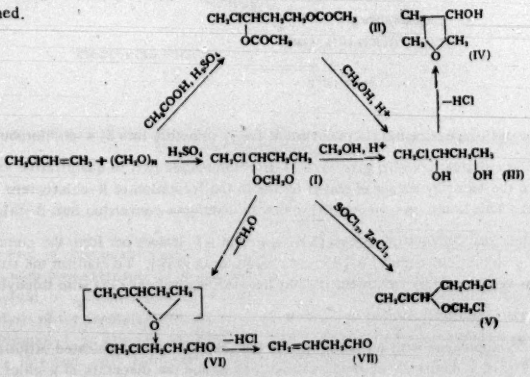
The reactions between olefins and formaldehyde have in recent years attracted the attention of chemists to a considerable extent [1].

The present paper deals with studies of the reactions of chloropropylenes (allyl chloride, 1-chloropropene, and 2-chloropropene) with formaldehyde. These reactions are of interest both in themselves, and because they provide an opportunity for relating reactivity with structural features of the molecule.

The reaction between allyl chloride and formaldehyde was studied by Price [2] who obtained 4-chloromethyldioxane-1, 3 in 45 % yield in the presence of concentrated sulfuric acid at 0°. Methanolysis of this compound leads to the formation of 3-hydroxytetrahydrofuran.

Our researches showed that the reactions between chloropropylenes and formaldehyde take place in harsher conditions and give lower yields than with propylene. We studied these reactions under various conditions: in the presence of concentrated sulfuric acid both without solvents and in various solvent media, and in the presence of chloromethylation agents (concentrated hydrochloric acid both in the presence and in the absence of zinc chloride).

In the reaction of ally chloride with formaldehyde in the presence of concentrated sulfuric acid in dichloroethane, the yield of 4-chloromethyldioxane-1, 3 (I) was 50%. If the reaction is carried out in glacial acetic acid, in addition to (I) a considerable amount of the diacetate of 4-chlorobutanediol-1,3 (II) is obtained.



Scheme 1

In order to confirm the structure of compounds (I) and (II), we subjected them to methanolysis. In both instances the corresponding diol was formed – 4-chlorobutanediol-1, 3 (III). This diol, which contains chlorine and a hydroxyl group in the 1,4 positions, is unstable and readily splits off HCl with ring closure and formation of 3-hydroxytetrahydrofuran (IV).

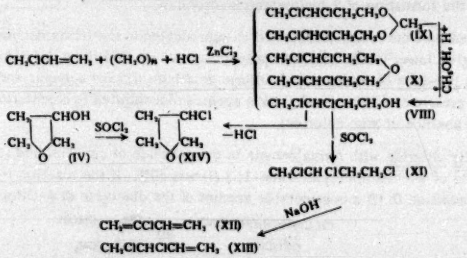
The action of thionyl chloride (in the presence of $ZnCl_2$) on 4-chloromethyldioxane results in the opening of the dioxane ring without evolution of formaldehyde; the resultant compound was identified as 2-chloromethoxy-1, 4-dichlorobutane (V).

It is known that 1, 3-alkyl dioxanes decompose to form dienes in good yields [1]. The decomposition proceeds smoothly in the presence of water vapor over suitable catalysts.

An investigation of the catalytic decomposition of 4-chloromethyldioxane-1, 3 over such catalysts in the temperature range 250-400° in various conditions (diluted with water vapor, and in a vacuum) showed that the result is not a chloro-substituted diene, but γ-chlorobutyraldehyde (VI), and the product formed by removal of hydrogen chloride from the latter is vinylacetic aldehyde (VII).

The above transformations are illustrated by Scheme 1.

The reaction between allyl chloride and formaldehyde in the presence of chloromethylation reagents, that is, in concentrated hydrochloric acid and in the presence of zinc chloride, results in other products. The main reaction products in this instance are the derivatives of the corresponding β-chlorohydrin, 3, 4-dichlorobutanol-1 (VIII), namely: its open chain formal (IX) and ether (X) in addition to a certain amount of the dichlorobutanol itself. If the reaction is carried out in the same conditions, but in the absence of zinc chloride, the reaction products do not contain the ether (X), but a certain amount of 4-chloromethyldioxane-1, 3 is formed.



Scheme 2

Methanolysis of the open-chain formal (IX) converts it fairly smoothly into 3, 4-dichlorobutanol-1 (VIII).

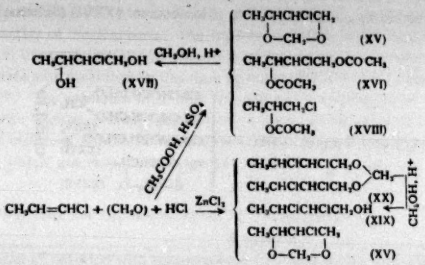
The action of thionyl chloride on (VIII) gives 1, 2, 4-trichlorobutane (XI) in quantitative yield. Removal of hydrogen chloride from the latter by means of NaOH results in the formation of β-chloroprene (XII) and 1, 2-dichlorobutane-3 (XIII). This latter, as is known [3] smoothly undergoes conversion into β-chloroprene.

When (VIII) is treated with dehydrating agents ($KHSO_4$ or $ZnCl_2$), it does not form the corresponding olefin, but splits off HCl with the formation of 3-chlorotetrahydrofuran (XIV). To confirm the structure of this last compound, it was synthesized by treatment of 3-hydroxytetrahydrofuran (IV) with thionyl chloride.

The above transformations are illustrated by Scheme 2.

The reaction of 1-chloropropene with formaldehyde in the presence of concentrated sulfuric acid in glacial acetic acid at 90° gave 4-methyl-5-chlorodioxane-1,3 (XV) and the diacetate of 2-chlorobutanediol-1, 3 (XVI). Methanolysis of (XVI) gave 2-chlorobutanediol-1, 3 (XVII). In contract with the diol obtained

from allyl chloride and formaldehyde (III), the diol (XVII) is a completely stable substance, as no favorable opportunity for ring closure exists in this instance. The acetate of 1-chloropronanol-2 (XVIII), which was the product of the reaction between acetic acid and 1-chloropropene without the participation of formaldehyde, was formed as a by-product.

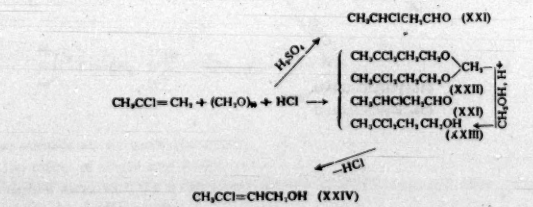


Scheme 3

In the reaction of 1-chloropropene with formaldehyde in the presence of chloromethylation agents the main reaction products are a β-chlorohydrin, 2, 3-dichlorobutanol-1 (XIX) and, chiefly, its formal (XX). The alkyl dioxane (XV) is formed only in a small amount. Methanolysis of the formal (XX) converts it into dichlorobutanol (XIX).

The above transformations of 1-chloropropylene are illustrated by Scheme 3.

In the reaction between 2-chloropropene and formaldehyde in the presence of concentrated sulfuric acid considerable resinification occurs even at low temperatures. The only substance which could be isolated was β-chlorobutyraldehyde (XXI) in a low yield (~ 10 %).

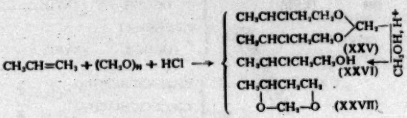


Scheme 4

In the presence of chloromethylation agents, however (concentrated hydrochloric acid), 2-chloropylene reacts vigorously with formaldehyde. The principal reaction products are the formal of 3, 3-dichlorobutanol-1 (XXII) in 53% yield, 3, 3-dichlorobutanol-1 itself (XXIII), and also a certain amount of β-chlorobutyraldehyde (XXI). Methanolysis of the formal (XXII) converts it into dichlorobutanol (XXIII). To confirm the structure of 3, 3-dichlorobutanol-1, an attempt was made to hydrolyze it by means of $CaCO_3$ with the aim of obtaining 3-ketobutanol-1. However, only 3-chlorocrotyl alcohol (XXIV) was isolated from the hydrolysis products, which was evidently formed by the removal of hydrogen chloride from 3, 3-dichlorobutanol. This also confirms the presence of two chlorine atoms at the third carbon atom of the latter.

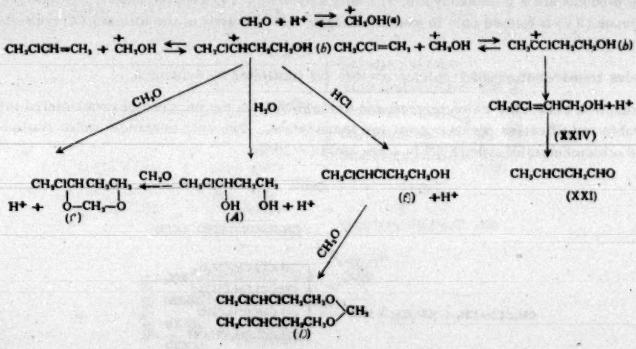
The transformation cycle for 2-chloropropylene is illustrated by Scheme 4.

In order to confirm that the reaction between olefins and formaldehyde in the presence of chloromethylation agents is a general one, resulting in the formation of β-chlorohydrins and their formals, an experiment with propylene was carried out. In these conditions propylene reacts very vigorously even at room temperature (there is a report of the possibility of such a reaction [5]); the main reaction products are 3-chlorobutanol-1 (XXVI) and its formal (XXV). A certain amount of 4-methyldioxane-1, 3 (XXVII) is also formed. The formal (XXV) is quantitatively converted by methanolysis into chlorobutanol (XXVI) (Scheme 5).



Scheme 5

The mechanism of the above reactions, which occur in the presence of strong acids, may be explained on the basis of the carbonium ion mechanism theory of acid catalysis [4] (Scheme 6).



Scheme 6

The acid supplies a proton for the formation of a carbonium ion (a) from formaldehyde. This then attacks the β-carbon atom in the olefin with the formation of an alcohol-carbonium ion (b). The carbonium ion (b) can then undergo the following transformations (by splitting off a proton); it can form a diol (A) by interaction with water, a β-chlorohydrin (B) by interaction with hydrogen chloride, and an alkyl dioxane-1, 3 (C) by interaction with formaldehyde. Further reactions of (A) and (B) with formaldehyde give an alkyl dioxane (C) and the formal of the β-chlorohydrin (D). In Scheme 6 this mechanism is shown as an example of the reactions of allyl chloride with formaldehyde, and the preparation of the compounds (III), (VIII), (I), and (IX) is illustrated. The mechanism is also quite applicable to reactions of other chloropropylenes.

The alcohol-carbonium ion (b) may also undergo regrouping into a β-unsaturated alcohol, which isomerizes to an aldehyde by the action of acids. In our opinion this is the mechanism for the formation of β-chlorobutyraldehyde (XXI) from 2-chloropropylene (see Scheme 6).

We represent the mechanism of the contact decomposition of 4-chloromethyldioxane-1, 3 (I) as follows: the dioxane (I) splits off formaldehyde with the formation of a compound containing an unstable four-membered ring, which is subsequently isomerized into γ-chlorobutyraldehyde (VI) (see Scheme 1).

In the study of the reactions between isomeric propylenes and formaldehyde in the presence of chloromethylation agents it was noted that they react at different rates; propylene itself reacts the most rapidly.

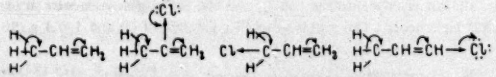
In this work we confined ourselves to determinations of only the relative rates for the different chloropropylenes under the same conditions, and to a comparison of these with the rate for propylene; it was not the intention to study the kinetics of the reactions. The relative reactivity experiments were performed under the same conditions: at constant initial concentrations of the olefin and formaldehyde and of hydrochloric acid. The reaction rate was measured by the time necessary for a definite percentage of the formaldehyde to be consumed. The reactions with allyl chloride and 1-chloropropene were carried out at 80 and 90°. The reactions with 2-chloropropene and propylene were carried out at 25°. In order to make possible a comparison of the results of the two series of experiments, we used the calculated temperature coefficient for the reaction, which was very close to two (see Table).

Relative Reaction Rates of Propylene and Chloropropylenes with Formaldehyde.

Temperature	Duration of reaction with formaldehyde (in minutes) for 25% conversion			
	Propylene	2-chloropropene	allyl chloride	1-chloropropene
25°	8.5	60.0	–	–
80	–	–	86.5	125.0
90	–	–	43.5	64.0

On the basis of these results the relative reactivities of propylene and its monochloro derivatives in the reaction with formaldehyde and hydrogen chloride may be expressed by the following sequence: propylene – 2-chloropropene – allyl chloride – 1-chloropropene = 100 : 143 : 2 : 1.3.

The different reactivities of the isomeric chloropropylenes and propylene may be qualitatively explained on the basis of modern electronic concepts. The structural features of the molecules of these compounds may be represented as follows:



In these compounds we meet the influence (in the static state) of at least three different effects [6]: the conjugation effect of single and double bonds – σπ-conjugation (I), the conjugation effect of the lone pair of the chlorine atom with the π-electrons of the double bond (II), and the negative induction effect of the chlorine atom, the I-effect (III).

In propylene there is only the effect (I), which determines the electronic shift in the molecule. In the allyl chloride molecule effects (I) and (III) are opposed. In the 1-chloropropene molecule effects (I) and (II) are opposed, while in the 2-chloropropene molecule the influence of effects (I) and (II) is additive. The resultant electron displacement in all these compounds has the same direction from the α- to the β-carbon atom, which is confirmed by the structure of the reaction products. The mutual influence of these effects determines only the magnitude of this displacement (and therefore the relative reactivity).

EXPERIMENTAL

A. Reaction of chloropropylenes with formaldehyde

If the reaction was carried out below the boiling point of chloropropylene, it was performed in a three-necked flask fitted with a mechanical stirrer, thermometer, and reflux condenser (Method A-1). At higher

temperatures the reaction was carried out in coppered rocking autoclaves of 1.7 and 3 liters capacity (Method A-2).

The reaction mass at the end of the reaction was poured into ice-cold water; the oily layer was separated off, and the aqueous acid layer was extracted with dichloroethane (or chloroform). The combined oily layers were then neutralized with 5 % Na_2CO_3 solution, dried over calcined potash and distilled under vacuum after removal of the unreacted chloropropylene and solvent.

B. Methanolysis of the reaction products

The methanolysis was performed in the presence of concentrated sulfuric acid (as catalyst) and excess of methyl alcohol. The reaction was carried out in a round-bottomed flask connected to a small rectifying column. The azeotrope of methylal and methyl alcohol was first collected. The calculated amount of anhydrous sodium acetate (for neutralization) was added to the reaction mixture, the liquid was heated to boiling, and then filtered to remove the precipitate of Na_2SO_4. The filtrate was then distilled under vacuum.

The starting chloropropylenes. Allyl chloride (b. p. 45°, n_D^{20} 1.4153) was obtained from the Semashko factory. 2-Chloropropene (b. p. 22.6°, $n_D^{6.5}$ 1.4040) and 1-chloropropene (a mixture of the cis- and trans-isomers, b. p. 32.2 – 36.7°, n_D^{20} 1.4055) were synthesized by removal of hydrogen chloride from 1, 3-dichloropropane by means of alcoholic alkali followed by fractionation on a column with 50 theoretical plates.

4-Chloromethyldioxane-1, 3 (I) was prepared by Method A-1. 300 g of paraformaldehyde (95%), 150 ml of concentrated H_2SO_4, 300 ml of dichloroethane, and 430 ml of allyl chloride (added in small portions) were stirred 3 hours at 40°. Yield 301.3 g (50.3%).

B. p. 58.5-59° at 8 mm, d_4^{20} 1.2103, n_D^{20} 1.4632. Literature data [2]: b. p. 80-83° at 20 mm, d_4^{20} 1.2115, n_D^{20} 1.4632.

3-Hydroxytetrahydrofuran (IV) and 4-chlorobutanediol-1, 3 (III)* were prepared by Method B from 225 g of (I), 175 ml of CH_3OH, and 18.3 g of concentrated H_2SO_4. The yields were 81.2 g (49.5 %) of (IV) and 10.7 g of (III).

(IV): b. p. 60-60.5° at 6 mm, d_4^{20} 1.0916, n_D^{20} 1.4480. Literature data [2]: b. p. 50° at 1 mm, d_4^{20} 1.090, n_D^{20} 1.4486.

(III): b. p. 113.5-114° at 6 mm, d_4^{20} 1.2250, n_D^{20} 1.4731, MR_D 28.51; Cal. 28.59.

Found %: Cl 27.84; OH 23.50 (phthalation). $C_4H_9O_2Cl$. Calculated %: Cl 28.49; OH 27.31.

4-Chlorobutanediol-1, 3 diacetate (II)* was prepared by Method A-2 from 95 g of paraformaldehyde (95%), 300 ml of allyl chloride, 100 ml of concentrated H_2SO_4, and 500 ml of glacial acetic acid. The experiment was carried out at 80° for 3 hours. The yields were 41 g (20.6%) of (I) and 170.4 g (28.1%) of (II). The properties of (II) are:

b. p. 107-108° at 7 mm, d_4^{20} 1.1843, n_D^{20} 1.4489, MR_D 47.21; Cal. 47.32.

Found %: C 45.85; H 6.34; Cl 17.10. M 206. $C_8H_{13}O_4Cl$. Calculated %: C 46.04; H 6.23; Cl 17.01. M 208.46.

The methanolysis of (II) also gave the compounds (III) and (IV).

2-Chloromethoxy-1, 4-dichlorobutane (V)* 40 g of (I), 70 g of $SOCl_2$ and 5 g of calcined $ZnCl_2$ were placed in a two-necked flask fitted with a reflux condenser and a dropping funnel. The mixture was heated 4.5 hours with gentle boiling. The reaction mass was separated from $ZnCl_2$ and distilled under vacuum.

The yield was 26 g (46.4 %) of (V):

* Compounds marked by an asterisk are described for the first time.

B. p. 96.5-97° at 8 mm, d_4^{20} 1.3263, n_D^{20} 1.4850, MR_D 41.35; Calc. 41.43.

Found %: Cl 55.38. M 194. $C_5H_9OCl_3$. Calculated %: Cl 55.58. M 191.38.

γ-Chlorobutraldehyde (VI)* and vinylacetaldehyde (VII)* The catalytic decomposition of (I) was carried out in the laboratory contact furnace over the usual catalyst used for the decomposition of 1, 3-alkyl dioxanes. The experimental conditions were: temperature 375°, feed rate of (I), 16.8 ml per 40 ml of catalyst per hour; feed rate of water, 3 volumes to 1 volume of (I). 40 g of (I) was passed. 140 ml of a liquid was obtained which did not separate into layers. 20.7 g of a mobile liquid with a pungent smell was distilled off from the reaction mass. A second distillation yielded 7.5 g of a fraction with b. p. 90-100°, d_4^{20} 0.8427, n_D^{20} 1.4300, which decolorized bromine in CCl_4, solution, gave the silver mirror reaction, and resinified rapidly on standing. The fraction was identified as vinylacetaldehyde (2, 4-dinitrophenyl hydrazone, m. p. 164°).

Found %: N 22.72 (Kjeldahl). $C_{10}H_{10}O_4N_4$. Calculated %: N 22.39.

The residue was extracted with chloroform. The extract was separated off, dried and distilled under vacuum. The yield was 1.5 g (18.5%) of (VII).

B. p. 72-72.5° at 57 mm, d_4^{20} 1.0864, n_D^{20} 1.4341, MR_D 25.52; Cal. 25.55.

Found %: Cl 33.21. C_4H_7OCl. Calculated %: Cl 33.30.
2,4-Dinitrophenyl hydrazone, m. p. 94° (from alcohol).
Found %: N 19.7. $C_{10}H_{11}O_4N_4Cl$. Calculated %: N 19.5.

3,4-Dichlorobutanol-1 (VIII)* its ether (X)* and the open-chain formal (IX)* were prepared by Method A-1.

300 ml of allyl chloride, 450 g of $ZnCl_2$, 200 ml of concentrated hydrochloric acid (36.7 %) and 150 g of paraformaldehyde (95% added in small portions) were taken for the reaction. The experiment lasted 3 hours at 25°, with hydrogen chloride passed continuously into the reaction flask.

a) 10.1 g (2%) of (VIII) was obtained.

B. p. 90-92° at 6 mm, d_4^{20} 1.2855, n_D^{20} 1.4825, MR_D 31.74; Cal. 31.93.

Found %: Cl 49.51; OH 11.52 (phthalation). $C_4H_8OCl_2$. Calculated %: Cl 49.65; OH 11.88.
3,5-Dinitrobenzoate with α-naphthylamine, m. p. 102° (from alcohol).

b) 180 g (58.4 %) of a mixture of (IX) and (X) was obtained, containing 60% of (IX) and 40% of (X).

Compound (X) has: b. p. 151-152° at 7 mm, d_4^{20} 1.2829, n_D^{20} 1.4904. MR_D 60.44; Calc. 60.25.

Found %: Cl 53.02. M 260. $C_8H_{14}OCl_4$. Calculated %: Cl 52.98. M 267.84.

Compound (IX) has: b. p. 154-157° at 4 mm, d_4^{20} 1.2948, n_D^{20} 1.4888. MR_D 66.40; Calc. 66.52.

Found %: C 35.85; H 5.11; Cl 47.49. M 287. $C_9H_{16}O_2Cl_4$. Calculated %: C 36.59; H 5.62; Cl 47.65. M 297.84.

180 g of a mixture of (IX) and (X) was subjected to methanolysis, 67.9 g of (VIII) and 40.7 g of (X) being obtained.

3-Chlorotetrahydrofuran (XIV)* a) 50 g of calcined $KHSO_4$ and 50 g of (VIII) were placed in a flask connected to a fractionating column, and the mixture heated on an oil bath. The yield was 19.5 g (52.5%) of (XIV).

B. p. 129.1-129.2° at 751 mm, d_4^{20} 1.1632, n_D^{20} 1.4530, MR_D 24.73; Cal. 24.98.

Found %: Cl 33.50. M 109. C_4H_7OCl. Calculated %: Cl 33.30. M 106.46.

b) 50 g of (IV) was placed in a flask fitted with a reflux condenser and a dropping funnel, and 42 ml of $SOCl_2$ was added. The yield was 10.1 g of (XIV).

1, 2, 4-Trichlorobutane (XI)* 50 g of $SOCl_2$ was placed in a double-necked flask fitted with a reflux condenser and a dropping funnel, and 38 g of (VIII) was added. The yield was 38 g of (XI).

B. p. 61-62.5° at 10 mm, d_4^{20} 1.3175, n_D^{20} 1.4820, MR_D 34.93; Cal. 35.27.

Found %: Cl 65.89. $C_4H_7Cl_3$. Calculated %: Cl 65.92.

β-Chloroprene (XII) and 1, 2-dichlorobutene-3 (XIII). 13.5 g of (XII) and 11 g of powdered NaOH were placed in a round-bottomed flask. The flask was connected to a distillation column and heated on an oil bath. The reaction started at 190°. A mixture of chlorinated compounds and water (b. p. 116-118°) was collected. After drying the product was fractionated.

a) Obtained 1.5 g (XII) b. p. 59-60°, d_4^{20} 0.9590, n_D^{20} 1.4600.

Found %: Cl 40.25. C_4H_5Cl. Calculated %: Cl 40.00.

Literature data [7]: b. p. 59.4°, d_4^{20} 0.9583, n_D^{20} 1.4583.

The β-chloroprene, with an addition of hydroquinone, polymerized after 10 days.

b) 3.1 g of (XIII) was obtained.

B. p. 122-123°, d_4^{20} 1.1583, n_D^{20} 1.4635. Literature data [8]: b. p. 122°, n_D^{20} 1.4641.

4-Methyl-5-chlorodioxane-1, 3 (XV)*, 2-chlorobutanediol-1, 3 diacetate (XVI)* and 1-chloropropanol-2 acetate (XVIII)* were prepared by method A-2 from 100 g of paraformaldehyde (95%), 280 ml of 1-chloropropane, 100 ml of concentrated sulfuric acid and 500 ml of glacial acetic acid. The mixture was stirred at 90° for 3 hours.

a) 41.3 g (25%) of (XV) was obtained.

B. p. 79-80° at 15 mm, d_4^{20} 1.1964, n_D^{20} 1.4611, MR_D 31.30; Cal. 31.24.

Found %: C 43.78; H 6.72; Cl 26.05. M 142.3. $C_5H_9O_2Cl$. Calculated %: C 43.92; H 6.63; Cl 25.93. M 136.46.

b) 43 g (8.5%) of (XVI) was obtained.

B. p. 92-94° at 7 mm, d_4^{20} 1.1724, n_D^{20} 1.4435, MR_D 47.18; Cal. 47.32.

Found %: C 45.85; H 6.84; Cl 17.28. M 208. $C_8H_{13}O_4Cl$. Calculated %: C 46.0; H 6.23; Cl 17.01. M 208.46.

c) 12.1 g of (XVIII) (a side-product) was obtained.

B. p. 42-44° at 20 mm, d_4^{20} 1.1459, n_D^{20} 1.4375, MR_D 31.23; Calc. 31.81.

Found %: C 43.66; H 6.50; Cl 26.20. M 130. $C_5H_9O_2Cl$. Calculated %: C 43.96; H 6.59; Cl 25.93. M 136.46.

2-Chlorobutanediol-1, 3 (XVII)* was prepared by the methanolysis of (XVI). 24.2 g of (XVI) gave 5.35 g of (XVII).

B. p. 100-102° at 8 mm, d_4^{20} 1.2406, n_D^{20} 1.4760, MR_D 28.21; Calc. 28.59.

Found %: Cl 28.13; OH 25.12 (phthalation). $C_4H_9O_2Cl$. Calculated %: Cl 28.49; OH 27.31.

2,3-Dichlorobutanol-1 (XIX)*, 4-methyl-5-chlorodioxane (XV)*, and the open-chain formal of 2,3-dichlorobutanol-1 (XX)* were prepared by Method A-1 from 115 g of paraformaldehyde (95%), 250 ml of 1-chloropropene, 400 g of anhydrous $ZnCl_2$, and 450 g of crystalline orthophosphoric acid. The experiment was carried out for 4 hours at 40° with a continuous stream of hydrogen chloride passed into the flask.

a) 33.4 g of a fraction with b. p. 70-76° at 10 mm was obtained; this was a mixture of compounds (XV) and (XIX). The fraction contained 9.7 g (2.3%) of (XIX) and 23.7 g (11.7%) of (XV).

b) 121.3 g (41.5%) of (XX) was obtained.

B. p. 145-147° at 6 mm, d_4^{20} 1.2703, n_D^{20} 1.4790, MR_D 66.52; Calc. 66.52.

Found %: C 36.42; H 5.62; Cl 47.5. M 296. $C_9H_{16}O_2Cl_4$. Calculated %: C 36.59; H 5.62; Cl 47.65. M 297.84.

40 g of the compound (XX) was subjected to methanolysis. 22.1 g (57.6%) of (XIX) was obtained.

B. p. 75-76° at 100 mm, d_4^{20} 1.2697, n_D^{20} 1.4731. MR_D 31.60; Calc. 31.93.

Found %: Cl 49.51; OH 11.55 (phthalation). $C_4H_8OCl_2$. Calculated %: Cl 49.65; OH 11.88. 3, 5-Dinitrobenzoate with α-naphthylamine melts at 98-100° (from alcohol).

β-Chlorobutyraldehyde (XXI). 50 g of paraformaldehyde (95%), 30 ml of concentrated H_2SO_4, and 100 ml of 2-chloropropene (added in small portions) were placed in a three-necked flask fitted with a reflux condenser, mechanical stirrer, and a dropping funnel. The duration of the experiment was 1.5 hours at 10°. Resinification occurred during the reaction. The yield of (XXI) was 14.3 g (10.2%).

B. p. 56-57° at 30 mm, d_4^{20} 1.0826, n_D^{20} 1.4351. 2, 4-Dinitrophenyl hydrazone, m. p. 77-78° (from alcohol). Literature data [5]: b. p. 28-32° at 13 mm. unstable.

β-Chlorobutyraldehyde (XXI), 2, 3-dichlorobutanol-1 (XXIII)*, and the open-chain formal of 2, 3-dichlorobutanol-1 (XXII)* were prepared by Method A-2. 150 g of paraformaldehyde (95%), 300 ml of 2-chloropropene and 1000 ml of concentrated hydrochloric acid (36.7%) were taken for the reaction. The mixture was heated with stirring 3 hours at 45°.

The yields were 40.5 g (12.7%) of (XXI), 195 g (53%) of (XXII), and 8.7 g (2%) of (XXIII).

The compound (XXIII) has the following properties:

B. p. 73-75° at 10.5 mm, d_4^{20} 1.2309, n_D^{20} 1.4650, MR_D 32.17; Calc. 31.93.

Found %: C 33.26; H 5.37; Cl 49.52; OH 11.70 (phthalation). $C_4H_8OCl_2$. Calculated %: C 33.56; H 5.59; Cl 49.65; OH 11.88. 3, 5-Dinitrobenzoate with α-naphthylamine melts at 105-106° (from alcohol).

The compound (XXII) has the following properties:

B. p. 123-125° at 4-5 mm, d_4^{20} 1.2575, n_D^{20} 1.4750, MR_D 66.18; Calc. 66.52.

Found %: C 36.24; H 5.36; Cl 47.48. M 296. $C_9H_{16}O_2Cl_4$. Calculated %: C 36.59; H 5.62; Cl 47.65. M 297.84.

Methanolysis of (XXII) by Method B gave (XXIII) in 68% yield.

3-Chlorocrotyl alcohol (XXIV). 25 g of (XXIII), 35 g of precipitated chalk, and 100 ml of water were placed in a flask fitted with a reflux condenser. The mixture was heated on an oil bath at 130° for 4 hours. The reaction liquid was filtered to remove the precipitate, dried, and distilled. 5.1 g (27.4%) of (XXIV) was obtained.

B. p. 54-56° at 10 mm, d_4^{20} 1.1135, n_D^{20} 1.4620. Literature data [10]: b. p. 52-53° at 9 mm, d_4^{20} 1.095, n_D^{20} 1.4652.

4-Methyldioxane-1, 3 (XXVII), 3-chlorobutanol-1 (XXVI) and the open-chain formal of 3-chlorobutanol-1 (XXV)* were prepared by Method A-2. 57.6 g of paraformaldehyde, 400 ml of concentrated hydrochloric acid, and 310 ml of propylene (87%) were taken for the reaction. The mixture was stirred 50 minutes at room temperature (25°).

a) 16.8 g (18.5%) of (XXVII) was obtained.

B. p. 115.3°, d_4^{20} 0.9758, n_D^{20} 1.4159. Literature data [1]: b. p. 116°, d_4^{20} 0.9748, n_D^{20} 1.4202.

b) 8.4 g (4.3%) of (XXVI) was obtained.

B. p. 69° at 17 mm, d_4^{20} 1.06415, n_D^{20} 1.4428. Literature data [11]: b. p. 170-180°.

c) 45.4 g (33.3%) of (XXV) was obtained.

B. p. 131.5° at 16.5 mm, d_4^{20} 1.08075, n_D^{20} 1.4499, MR_D 56.54; Cal. 56.78.

Found %: Cl 30.62. $C_9H_{18}O_2Cl_2$. Calculated %: Cl 30.96.

The formal (XXV) was converted by methanolysis into (XXVI) in practically quantitative yield.

Determination of the Relative Reactivities of Chloropropylenes and of Propylene

The experiments with allyl chloride and 1-chloropropene were carried out at 80 and 90° in glass ampoules of 20 ml capacity which were placed in a rocking air-thermostat. Each ampoule contained 1 g of paraformaldehyde (calculated as 100%), 3 ml of the olefin, and 4 ml of concentrated hydrochloric acid (36.7%). At the end of a definite time the contents of the ampoule were quantitatively transferred into a measuring flask, and the formaldehyde content was determined.

The experiments with propylene and 2-chloropropene were carried out at 25° in a coppered autoclave of 250 ml capacity. The autoclave contained 20 g of paraformaldehyde (calculated as 100%; previously depolymerized), 55 g of the olefin, and 80 ml of concentrated hydrochloric acid. At definite time intervals samples were taken from the autoclave and analyzed for formaldehyde content.

SUMMARY

1. A study was made of the reactions between chloropropylenes and formaldehyde in the presence of concentrated hydrochloric acid, and also of some transformations of the main reaction products.

2. The contact decomposition of 4-chloromethyldioxane-1, 3 (the main product of the reaction between allyl chloride and formaldehyde) leads not to the formation of a chloro-substituted diene, but of σ-chlorobutyraldehyde and its dehydrochlorination product.

3. The main products of the reaction between chloropropylenes and formaldehyde in the presence of hydrogen chloride are β-chlorohydrin (dichlorobutanol) derivatives.

4. The reactions of 3, 4-dichlorobutanol, including those leading to the formation of β-chloroprene were studied.

5. The formation of all the reaction products is satisfactorily explained by the application of the carbonium ion mechanism of acid catalysis to the reactions.

6. The relative reactivities of propylene and its monochloro derivatives in the reaction with formaldehyde in the presence of hydrogen chloride were determined.

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CONDENSATION OF DIENE COMPOUNDS WITH METHYL ACRYLATE. SYNTHESIS OF HYDROAROMATIC ALCOHOLS AND HYDROCARBONS

N. P. Sapov

In the previous papers the possibility of the preparation of hydroaromatic alcohols and hydrocarbons of very varied structures from the homocyclization products of 1, 3-diene compounds with α, β-unsaturated carbonyl compounds, acids and their derivatives was discussed [1-3]. In a continuation of work in this direction, we studied the condensation of divinyl, piperylene, isoprene, dipropenyl, diisopropenyl, cyclopentadiene, cyclohexadiene and chloroprene with methyl acrylate, and from the reaction products of this condensation – the esters of cyclohexene carboxylic acid and its homologs – we prepared a number of alcohols and hydrocarbons.

The literature contains data on the condensation of some dienes with methyl acrylate. Piperylene and methyl acrylate gave the methyl ester of 2-methylcyclohexene-3-carboxylic acid, the structure of which was proved by its conversion into o-phthalic acid by dehydrogenation and oxidation [4]. Isoprene gave the methyl ester of 4-methylcyclohexene-3-carboxylic acid. The action of Grignard reagent on it gave α-terpineol [5].

We previously prepared the methyl esters of 3-cyclohexene-3-carboxylic acid and 4-chlorocyclohexene-3-carboxylic acid by alcoholysis of the nitriles of the acids [6].

The constants of the cyclohexene carboxylic esters are shown in Table 1, from which it is seen that increase in the number of radicals results in a regular rise of boiling points, fall of specific gravity, and has little effect on the refractivity. The isoprene derivatives have higher boiling points and greater specific gravities and refractive indices than the piperylene derivatives. All these esters are colorless liquids with a characteristic pleasant odor. The cyclic diene derivatives have an odor which differs from that of the other esters.

The action of CH_3MgI on the cyclohexene carboxylic esters (3 moles to 1 mole of ester) gave tertiary aromatic alcohols, some of which were synthesized from the corresponding ketones, and had also been synthesized by other workers by different methods. The constants of the alcohols are shown in Fig. 2, from which it is seen that the different methods yielded alcohols which showed practically no difference from each other.

The tertiary alcohols were dehydrated by heating with acetic anhydride. The properties of the hydroaromatic hydrocarbons so obtained are shown in Table 3.

The dehydration of dimethyleneendoethylenecyclohexenyl carbinol resulted in removal of the endoethylene bridge, and the reaction products were cumene and ethylene. The latter was identified as the dibromide.

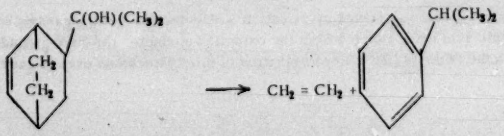
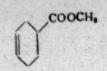
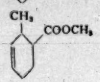
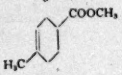
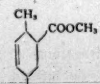
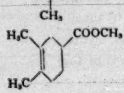
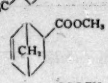
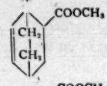
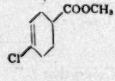
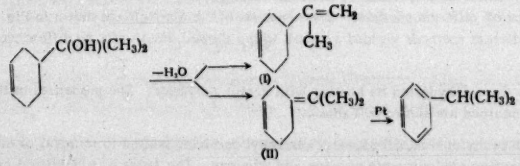


TABLE 1

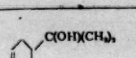
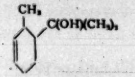
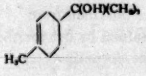
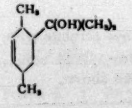
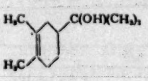
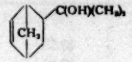
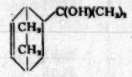
Substance	Boiling Point (20 mm)	d_4^{20}	n_D^{20}	MR	
				Found	Calculated
	78.5—79.5° 79.5 [6]	1.0130 0.9946	1.4621 1.4650	38.05 38.96	38.13 38.13
	85—86	0.9857	1.4602 1.432 (?) [4]	42.86	42.74
	93—93.5 83—86 (13 mm) [5]	0.9906 —	1.4636 —	42.92 —	42.74 —
	96—97	0.9776	1.4628	47.39	47.37
	105.5—106.5	0.9669	1.4722	47.75	47.37
	85—85.5	1.0240	1.4745	42.00	41.81
	106—106.5	1.0600	1.4870	45.10	45.16
	115—116 117.5—118.5 [6]	1.1650 1.1623	1.4898 1.4878	43.33 43.25	43.00 43.00

There can be no doubt concerning the structure of the condensation product of divinyl and methyl acrylate. The structure of the alcohol obtained from it is also quite definite. The dehydration of the same alcohol could give two hydrocarbons:

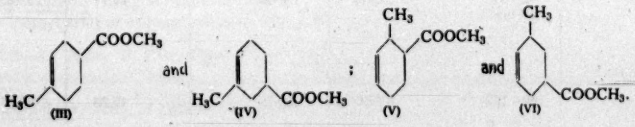


The structure of the compound was proved by oxidation with potassium permanganate, acetone, cyclohexenone, and succinic acid being isolated from the oxidation products. On these grounds the hydrocarbon obtained was given the Formula (II). Dehydrogenation of this hydrocarbon over Pt gave cumene.

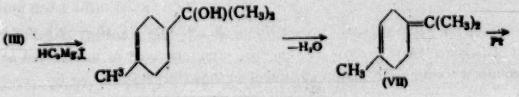
TABLE 2

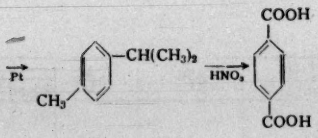
Substance	Boiling Point (20 mm)	d_4^{20}	n_D^{20}	MR		OH (in %)	
				Found	Calculated	Found	Calculated
	95—96° 95.5—96[1]	0.9489 0.9479	1.4826 1.4826	42.17 42.21	42.62 42.62	12.06	12.12
	102—103 110—112[1] (30 mm)	0.9405 0.9404	1.4827 1.4792	46.81 46.53	47.24 47.24	10.95	11.02
	110—111 120—122[2] (30 mm)	0.9344 0.9350	1.4822 1.4831	47.12 47.17	47.24 47.24	11.17	11.02
	112—113 111.5—112.5[1]	0.9364 0.9367	1.4840 1.4844	51.34 51.34	51.86 51.86	10.21	10.10
	120—121 121—121.5[1]	0.9380 0.9370	1.4881 1.4882	51.69 51.76	51.85 51.85	9.74	10.10
	92—93	0.9824	1.4897	44.78	45.04	11.44	11.17
	113—114	1.0020	1.5050	49.20	49.66	10.51	10.23

In the condensation of methyl acrylate with isoprene and piperylene, the formation of two isomeric esters might be expected in each instance:



The structure of the condensation products of the ester with isoprene and piperylene was established according to the following Scheme (for isoprene):

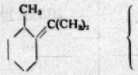
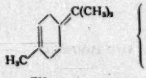
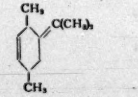
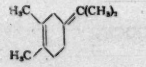
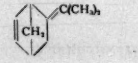




As the results of a series of reactions, the first yielded terephthalic, and the second, o-phthalic acid. Therefore the substance obtained from isoprene must have Formula (III), and the substance obtained from piperylene, Formula (V). The potassium permanganate oxidation of the hydrocarbon obtained by dehydration of dimethyl-(4-methylcyclohexenyl-3) carbinol yielded only acetone. On these grounds the Formula (VII) was attributed to the hydrocarbon derived from isoprene.

There can be no doubt concerning the structures of the condensation products of methyl acrylate with the other diene hydrocarbons. The structures of the hydroaromatic hydrocarbons obtained from them were not determined. They are evidently analogous to that found for the two substances described above.

TABLE 3

Substance	Boiling Point (760 mm)	d_4^{20}	n_D^{20}	MR Found	MR Calculated
	155—158°	0.8523	1.4805	41.03	40.63
	151—155°[1]	0.8467	1.4774	40.80	40.63
	171—172	0.8564	1.4792	45.22	45.25
	172—174°[1]	0.8544	1.4785	45.18	45.25
	176—178	0.8493	1.4830	45.81	45.25
	176—177°[1]	0.8498	1.4830	45.78	45.25
	92—94 (50 mm)	0.8575	1.4800	49.77	49.86
	160—162	0.8793	1.4875	49.20	49.86
	71—73 (20 mm)	0.9179	1.4970	42.79	43.04

It must be noted that the hydroaromatic hydrocarbons usually had a boiling range of 2-3°. Possibly they consisted of mixtures of isomers; therefore our data on their structure must be interpreted as data on the structure of the hydrocarbon forming the main constituent of the substance.

EXPERIMENTAL

Condensation of Dienes With Methyl Acrylate

The methyl acrylate used had the following constants:

B. p. 80-81°, d_4^{20} 0.9520, n_D^{20} 1.4065. Literature data [9]: b. p. 80°, d_4^{20} 0.9535, n_D^{20} 1.4040.

The condensation took place in sealed glass tubes in toluene solution in the presence of hydroquinone on heating for 12 hours at 140-150°.

Divinyl. 10.8 ml of divinyl and 17.2 ml of methyl acrylate in 20 ml of toluene gave, after distillation of the reaction mixture under vacuum at 20 mm, 18 g (64%) of the methyl ester of cyclohexene 3-carboxylic acid and 1.5 g of resinous material.

Found %: C 68.73; H 8.92; CH_3O 22.01. $C_7H_9O(OCH_3)$. Calculated %: C 68.54; H 8.62; CH_3O 22.14.

Piperylene. 27.2 g of piperylene (technical 90% grade) and 17.2 ml of methyl acrylate in 30 ml of toluene gave 15.2 g (80%) of the methyl ester of 2-methylcyclohexene-3-carboxylic acid and 2.4 g of resin.

Found %: C 69.84; H 9.02; CH_3O 19.87. $C_8H_{11}O(OCH_3)$. Calculated %: C 70.10; H 9.19; CH_3O 20.12

Isoprene. 13.6 g of isoprene and 17.2 g of methyl acrylate in 20 ml of toluene gave 26 g (84%) of the methyl ester of 4-methylcyclohexene-3-carboxylic acid and 1.3 g of resin.

Found %: C 70.38; H 8.96; CH_3O 19.74. $C_8H_{11}O(OCH_3)$. Calculated %: C 70.10; H 9.15; CH_3O 20.12 .

Dipropenyl. 32.8 g of dipropenyl (technical grade) and 17.2 g of methyl acrylate in 30 ml of toluene gave 18.4 g (54%) of the methyl ester of 2, 5-dimethylcyclohexene-3-carboxylic acid and 1.7 g of resin.

Found %: C 71.77; H 9.33; CH_3O 18.15. $C_9H_{13}O(OCH_3)$. Calculated %: C 71.39; H 9.58; CH_3O 18.44.

Diisopropenyl. 12.3 g of diisopropenyl and 12.9 g of methyl acrylate in 15 ml of toluene gave 8.5 g (39%) of the methyl ester of 3, 4-dimethylhexene-3-carboxylic acid and 0.7 g of resin.

Found %: C 71.58; H 9.38; CH_3O 18.15. $C_9H_{13}O(OCH_3)$. Calculated %: C 71.39; H 9.58; CH_3O 18.44.

Cyclopentadiene. 6.6 g of cyclopentadiene and 8.6 g of methyl acrylate in 10 ml of toluene gave 7.2 g (78%) of the methyl ester of endomethylenecyclohexene-3-carboxylic acid and 0.5 g of resin.

Found %: C 70.88; H 7.90; CH_3O 20.78. $C_8H_9O(OCH_3)$. Calculated %: C 71.03; H 7.94; CH_3O 20.39.

Cyclohexadiene. 16 g of cyclohexadiene and 17.2 g of methyl acrylate in 20 ml of toluene gave 10.6 g (32%) of the methyl ester of endoethylenecyclohexene-3-carboxylic acid and 0.8 g of resin.

Found %: C 72.16; H 8.39; CH_3O 18.98. $C_9H_{11}O(OCH_3)$. Calculated %: C 72.26; H 8.49; CH_3O 18.67.

Chloroprene. 17.8 g of chloroprene, 17.2 g of methyl acrylate, and 30 ml of toluene were taken for the condensation. The condensation products were distilled in steam together with the toluene; 7 g of polymer remained in the distillation flask. The toluene solution of the condensation product was fractionated under vacuum after being dried with $CaCl_2$. Toluene was distilled off at 85 mm, then the pressure was lowered to 20 mm and the ester was distilled; 14 g (40%) of the methyl ester of 4-chlorocyclohexene-3-carboxylic acid was obtained.

Found %: Cl 21.97, 22.29; CH_3O 17.13. $C_7H_9OCl(OCH_3)$. Calculated %: Cl 20.31; CH_3O 17.77.

Preparation of Tertiary Alcohols

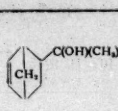
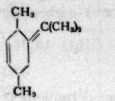
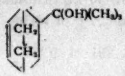
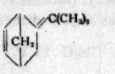
To a solution of the organomagnesium compound, prepared from 0.25 g-atom of magnesium and 0.28 mole of methyl iodide in 100 ml of anhydrous ether, 0.1 mole of the appropriate condensation product of a diene with methyl acrylate dissolved in 50 ml of ether was added with mechanical stirring and cooling. The mixture was allowed to stand 1 hour and warmed 2 hours, then left overnight. The organomagnesium complex was decomposed by the usual method. The ether solution of the tertiary alcohol was dried by calcined Na_2SO_4 and distilled. The alcohol yield was 50-65% calculated on the ester taken. The constants of the alcohols obtained are shown in Table 2. The hydroxyl group content of all the alcohols was determined by Terentyev's Method. The results are shown in Table 2.

Preparation of Hydroaromatic Hydrocarbons

The tertiary alcohols were dehydrated by heating them with fifty percent excess of acetic anhydride in sealed tubes for 6 hours at 200°. The hydrocarbon yields were 50-60%.

The analytical data for the alcohols and hydrocarbons obtained for the first time are shown in Table 4.

TABLE 4

Substance	Found %		Calculated %		Substance	Found %		Calculated %	
	C	H	C	H		C	H	C	H
	78.79	10.40	78.90	10.59		87.78 87.88	12.00 11.86	87.93	12.07
	79.39	10.80	79.46	10.91		89.40 89.21	10.62 10.42	89.49	10.51

Pressure was observed when the tubes were opened after heating of 6.5 g of dimethyl-(2, 5-endoethylene-cyclohexene-3-yl) carbinol with 6 g of acetic anhydride. Some of the tubes were previously cooled by a mixture of ice and salt, and the gas evolved when they were opened was passed into bromine-dibromoethane was formed:

B. p. 132-132.5°, n_D^{20} 1.5378. Literature data [10]: b. p. 131.7°, n_D^{20} 1.5379.

The residue yielded 2.9 g (50%) of cumene:

B. p. 51-52.5° (20 mm), d_4^{20} 0.8628, n_D^{20} 1.4932. Literature data [11]: b. p. 152.4°, d_4^{20} 0.8618, n_D^{20} 1.4915.

Oxidation of the substance by 25% HNO_3 gave benzoic acid with m. p. 119.5-120° [10].

2.4 g of the hydrocarbon obtained by dehydration of dimethyl-(4-methylcyclohexene-3-yl) carbinol was shaken 6 hours with 5% potassium permanganate solution in the presence of magnesium sulfate. The oxidation required 13.2 g of permanganate. The solution was then distilled in steam. Treatment of part of the distillate with an acetic acid solution of 2,4-dinitrophenylhydrazine gave a characteristic precipitate of acetone dinitrophenylhydrazone, m. p. 125-125.5° [12].

Found %: N 23.93, 23.62. $C_9H_{10}O_4N_4$. Calculated %: N 23.53.

The residue in the flask, after filtration and distillation in steam, was evaporated to a small volume and acidified with sulfuric acid. Carbon dioxide was evolved. No significant amounts of organic acids could be extracted from the liquid by repeated treatment with ether.

2.4 g of the hydrocarbon obtained by the dehydration of dimethyl-(cyclohexene-3-yl) carbinol was oxidized by 5% potassium permanganate solution (12.3 g) in the conditions described above. The solution was distilled in steam. The upper distillate layer was distilled after being separated and dried over $CaCl_2$. A substance with n_D^{20} 1.4768 was obtained. When this was treated with an acetic acid solution of p-nitrophenylhydrazine, a yellow precipitate of Δ^3-cyclohexenone p-nitrophenylhydrazone was formed, with m. p. 202-203°.

Found %: N 17.95, 18.00. $C_{12}H_{13}O_2N_3$. Calculated %: N 18.17.

Treatment of the lower distillate layer with an acetic acid solution of 2, 4-dinitrophenylhydrazine gave acetone 2, 4-dinitrophenylhydrazone, m. p. 125°.

Found %: N 23.51, 23.36. $C_9H_{10}O_4N_4$. Calculated %: N 23.53.

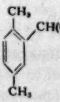
The residue in the flask, after filtration and distillation in steam, was evaporated to a small volume and acidified with sulfuric acid. Repeated treatment of the liquid with ether yielded succinic acid, m. p. 180° (from water).

Found %: C 40.75; H 5.45. $C_4H_6O_4$. Calculated %: C 40.77; H 5.13.

Dehydrogenation of the Hydroaromatic Hydrocarbons

The hydroaromatic hydrocarbons were dehydrogenated over platinized activated carbon at 325-350° by Zelinsky's Method. Aromatic hydrocarbons were obtained after a single pass. The constants are compared with the literature data in Table 5.

TABLE 5

Substance	Boiling Point (760 mm)	d_4^{20}	n_D^{20}	MR	
				Found	Calculated
	152—153°	0.8588	1.4885	40.35	40.16
	152.4°[11]	0.8616	1.4915	40.43	40.16
	177—179	0.8750	1.5003	45.14	44.78
	178.3°[11]	0.8766	1.5006	44.56	44.78
	175—177	0.8568	1.4932	45.54	44.78
	177.2°[11]	0.8573	1.4909	45.33	44.78
	85—86.5 (20 мм)	0.8669	1.4944	49.82	49.60

The analysis of an aromatic hydrocarbon obtained for the first time, 1, 4-dimethyl-2-isopropylbenzene, is given below.

Found %: C 89.46, 88.94; H 10.99, 11.22. $C_{11}H_{16}$. Calculated %: C 89.12; H 10.88.

The first three aromatic hydrocarbons were oxidized by 25% HNO_3 in sealed tubes. Oxidation of cumene gave benzoic acid with m. p. 119-120°. Oxidation of o-cymene gave o-phthalic acid with m. p. 184.5-185.5°. The phthalic anhydride obtained from it by means of acetic anhydride melted at 130.8°, which agreed with the literature data [10]. The oxidation of p-cymene gave terephthalic acid, the methyl ester of which (prepared in the usual way in the presence of H_2SO_4) melted at 140° [10].

SUMMARY

1. The condensation of methyl acrylate with divinyl, piperylene, isoprene, dipropenyl, diisopropenyl, cyclopentadiene-1, 3, cyclohexadiene-1, 3 and chloroprene was studied, and the methyl esters of 2, 5-dimethyl-3, 4-dimethyl-2, 5-endomethylene- and 2, 5-endoethylenecyclohexene-3-carboxylic acids were prepared for the first time.

2. By the action of methylmagnesium iodide on the condensation products of cyclopentadiene and cyclohexadiene-1, 3 and methyl acrylate, dimethyl-(2, 5-endomethylenecyclohexene-3-yl) carbinol and dimethyl-(2, 5-endoethylenecyclohexene-3-yl) carbinol, not previously described in the literature, were prepared.

3. The structure of the condensation products of methyl acrylate with piperylene and isoprene has been established.

4. A series of hydroaromatic hydrocarbons was obtained by the dehydration of tertiary alcohols, and the structure of two of them established.

5. It was shown that the dehydration of dimethyl-(2, 5-endoethylenecyclohexenyl-3) carbinol results in the removal of an ethylene molecule, with the formation of cumene.

6. The dehydrogenation of some hydroatomatic hydrocarbons over platinum was studied. 2, 5-Dimethyl-1-isopropyl benzene, not described in the literature, was prepared.

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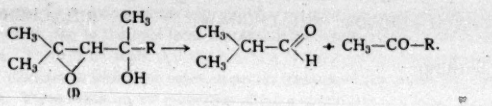
* T. p. = C. B. translation pagination.

INVESTIGATIONS OF OXIDO (EPOXY) COMPOUNDS

V. THE MECHANISM OF THE DECOMPOSITION OF α, β-ALCOHOL OXIDES OF THE ALIPHATIC SERIES BY THE ACTION OF ZINC CHLORIDE AND AQUEOUS SOLUTIONS OF MINERAL ACIDS

V. I. Pansevich - Kolyada

In the previous communication [1] it was shown that α, β-epoxy alcohols – 2, 4, 5-trimethyl-oxido-2, 3-hexanol-4 and 2, 4-dimethyl oxido-2, 3-decanol-4 – decompose by the action of zinc chloride to form isobutyraldehyde and the corresponding ketones:



(I)

A similar decomposition was previously observed for glycidol and some aryl-substituted α, β-epoxy alcohols at fairly high temperature in the presence of catalysts [2-6], by the action of organomagnesium compounds [7-9], and of phenyllithium [9, 10]. There are isolated reports of the decomposition of phenyl-substituted epoxy alcohols in the air [7, 9, 10] and in a desiccator over dehydrating agents [11].

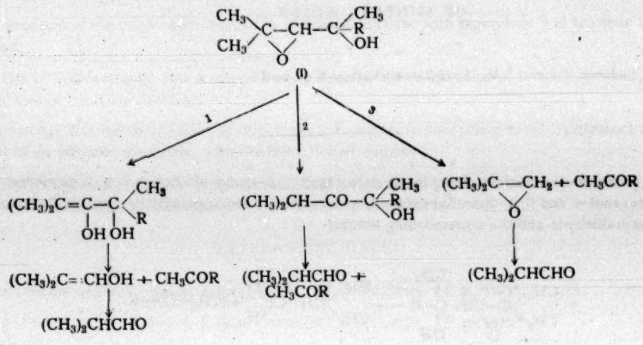
In the present investigation the behavior of five more α, β-epoxides – 2, 4-dimethyl-oxido-2, 3-octanol-4 (I, R = CH_3), 2, 4-dimethyl-oxido-2, 3-hexanol-4 (I, R = C_2H_5), 2, 4-dimethyl-oxido-2, 3-heptanol-4 (I, R = C_3H_7), 2, 4-dimethyl-oxido-2, 3-octanol-4 (I, R=C_4H_9), and 2, 4, 7-trimethyl-octanol-4 (I, R = iso-C_6H_{11}) – was studied under the action of anhydrous zinc chloride and dilute acid solutions.

All the above alcohol opoxides were obtained by oxidation of the corresponding unsaturated tertiary alcohols by acetyl hydroperoxide. These substances, like the alcohol opoxides 2, 4, 5-trimethyl-oxido-2, 3- hexanol-4 and 2, 4-dimethyl-oxido-2, 3-decanol-4, decompose under the action of anydrous zinc chloride to form isobutyraldehyde and the corresponding ketones: acetone, methyl ethyl ketone, methyl n-propyl ketone, methyl n-butyl ketone, and methyl isoamyl ketone.

A similar reaction occurs when the alcohol epoxides are mixed with dilute solutions of sulfuric or hydrochloric acids at room temperature, and more rapidly on heating. The same reaction occurs when the alcohol epoxides boiled with pure water. It should be noted that the decomposition rate of the alcohol epoxides decreases with increasing molecular weight.

This is apparently related to the solubility of the alcohol epoxides in water, which also decreases with increase of molecular weight. In the decomposition of α, β-epoxides, in addition to isobutyraldehyde and the corresponding ketones, small amounts of substances of higher molecular weight are also formed, the analysis of which corresponds to the formulas of the original alcohol epoxides. However, in their physical constants and properties they differ greatly from the original epoxides. These substances contain hydroxyl groups, do not react with semicarbazide, and yield a mixture of 2, 4-dinitrophenylhydrazones. They are apparently isomerization products of the alcohol epoxides.

All the aliphatic α, β-epoxy alcohols studied, containing a tertiary alcohol group, and also some alcohol epoxides with a phenyl group, are stable when kept under normal conditions. They are also unchanged by prolonged heating with aqueous ammonia solution, with diethylamine, and with dilute caustic soda solution. However, they are extremely unstable in the presence of zinc chloride, in aqueous solutions of acids, and in pure water, while 2-methyl-4-phenyl-oxido-2, 3-pentanol-4 is unstable even when kept in a desiccator over dehydrating agents [11]. In these quite different conditions the α, β-epoxides undergo decomposition of the same type with the formation of isobutyraldehyde and the corresponding ketones. There is no doubt that in all these cases unstable intermediate substances of one type are formed, and these give the above carbonyl derivatives upon decomposition. The whole mechanism of this process is undoubtedly very complex. However, the separate stages of the decomposition of α, β-epoxy alcohols may be represented by one of the following schemes:



The third scheme is improbable.

It is known [12, 13] that α-oxides are very easily isomerized to carbonyl compounds by anhydrous zinc chloride; it is therefore very unlikely that a carbon-carbon bond would be broken in the presence of this reagent while the epoxy ring is retained. Changes in the epoxy ring are to be expected first. Another objection to the third scheme is the formation of isobutyraldehyde when the alcohol opoxides are boiled with aqueous acids or water. If the decomposition followed this scheme, the aqueous medium should contain not isobutyraldehyde but isobutylene glycol, since isobutylene oxide, as was shown by Eltekov [14], combines vigorously with water even at room temperature. However, no isobutylene glycol was found in the reaction products.

The second scheme requires the preliminary isomerization of α, β-opoxides to α-keto alcohols, which then decompose.

Numerous papers [15-47] on the α-keto alcohols show that these compounds are rather stable even in harsh conditions. Most of them undergo isomeric conversions by the action of various reagents, but we did not find a single indication of the decomposition of α-keto alcohols. Only when benzoin and its derivatives are heated with alcoholic alkali, the carbon-carbon bond is broken with the formation of alcohols and acids [48-51].

These facts are sufficient for the second scheme to be regarded as not corresponding to reality. An objection to this scheme is also provided by the properties of 2-methyl-4-phenyl-oxido-2, 3-pentanol-4, which decomposes into acetophenone and isobutyraldehyde in very mild conditions [11]. If this epoxide was previously isomerized to the α-ketol, the latter would hardly be decomposed in a desiccator over H_2SO_4, $CaCl_2$ and P_2O_5.

The first scheme is more probable. α, β-Epoxy alcohols containing a tertiary alcohol group are isomerized to dienols by the action of zinc chloride, aqueous acid solutions, and on boiling with water.

The dienols, being apparently very unstable, decompose into ketones and a substituted vinyl alcohol which then isomerizes to isobutyraldehyde. In the case of 2-methyl-4-phenyl-oxido-2, 3-pentanol-4 this process takes place at room temperature in a desiccator over dehydrating agents [11].

The possibility is also not excluded that α, β-epoxy alcohols in the liquid state consist of an equilibrium mixture of the epoxy and enol forms with the equilibrium shifted very strongly toward the epoxy form. Under certain conditions the enol form is decomposed, which results in further enolization of the opoxy form. Heat, and the presence of hydrogen ions and of certain other substances, greatly accelerate these transformations.

The possibility of enolization of the three-membered epoxide ring was demonstrated by us in a paper on the properties of the α-oxides of propenyl phenolic derivatives [52]. This is also supported by work on the catalytic isomerization of the α-oxide ring to enols [53].

In our view, enolization takes place not only in alcohol epoxides, but in other compounds with three-membered oxide rings.

The α-oxides, starting with their first representative, ethylene oxide, are known to show unsaturated behavior, which, however, does not follow from the ring structure which was proposed [54-56] and subsequently confirmed [57-60] for these compounds. This contradiction remains unexplained to the present day. Possibly the conversion of α-oxides to enols is the reason for the discrepancy between the chemical properties which they display with different reagents, and their structure. Because of this transformation they act as unsaturated compounds with addition reactions characteristic of the latter. Isomerization of the α-oxide ring to the enol form is probably the intermediate phase in many of the reactions of α-oxides. There is no doubt that the structure of the α-oxides adjacent to the oxide ring, the radicals, and the medium in which the reaction occurs, determine the possibility and the rate of these transformations. These views on the properties of the α-oxide ring are in agreement with a whole series of reactions of the α-oxides which take place in an acid medium and on heating. Some contradictions are found in isolated reactions in an alkaline medium.

EXPERIMENTAL

2, 4-Dimethyl-Oxido-2, 3-Pentanol-4 (I, R = CH_3)

Preparation. The epoxy alcohol was prepared by oxidation of 2, 4-dimethylpenten-2-ol-4, which was synthesized from mesityl oxide and methylmagnesium chloride.

B. p. 75° (68 mm) [61, 62], n_D^{20} 1.4380, d_4^{20} 0.8399, MR_D 35.62; Calc. 35.58.

To 62 g of the alcohol in 130 ml of ether at 20-25° 46 g of 91% acetyl hydroperoxide was added. Heat was evolved during the oxidation. After two days the reaction products were treated as described previously [1] and dried over $MgSO_4$.

Vacuum distillation yielded 51 g of a mobile liquid with a pleasant but pungent odor. The substance is readily soluble in cold water and organic solvents. Aqueous solutions turn turbid after some time owing to decomposition of the alcohol epoxide and formation of isobutyraldehyde. The alcohol epoxide displaces iodine from aqueous potassium iodide solution; it rapidly decolorizes 1% permanganate solution. It contains active hydrogen.

B. p. 49-52° (15 mm) n_D^{20} 1.4165, d_4^{20} 0.9484, MR_D 35.5; Calc. 35.62.

Found %: C 60.00; H 10.37. $C_7H_{14}O_2$. Calculated %: C 60.00; H 10.76.

Decomposition of 2, 4-dimethyl-oxido-2, 3-pentanol-4 in sulfuric acid solution. 10 g of the alcohol epoxide was added to 20 ml of water containing 0.2 g of concentrated sulfuric acid. Heat was evolved immediately upon mixing and an odor of isobutyraldehyde was given off. The solution, homogeneous at first, became turbid, and a small layer of a liquid sparingly soluble in water floated up. The mixture was

heated 2 hours on the boiling water bath, the sulfuric acid was neutralized by potash, and the reaction products were extracted with ether, dried by $MgSO_4$, and distilled under normal pressure. The fraction boiling at 46-64° was collected in semicarbazide solution.

The semicarbazone was soon formed, which melted at 187°. A sample mixed with acetone semicarbazone gave no depression of melting point. The 64-85° fraction was collected in an alcoholic solution of dimedone. On the next day a crystalline addition product with m. p. 149-150° was obtained. A sample mixed with the addition product of dimedone and isobutyraldehyde gave no depression of melting point [11]. In addition to acetone and isobutyraldehyde, the high-boiling products were distilled at 191-211° (732 mm). The substances in this fraction contained active hydrogen, did not form a semicarbazone, and formed a mixture of 2, 4-dinitrophenylhydrazones.

2, 4-Dimethyl-Oxido-2, 3-Hexanol-4 (I, R = C_2H_5)

Preparation. The epoxy alcohol was prepared by the oxidation of 2, 4-dimethylhexen-2-ol-4, which was synthesized from ethylmagnesium bromide and mesityl oxide.

B. p. 53-54° (10 mm) [63], n_D^{20} 1.1445, d_4^{20} 0.8483, MR_D 40.16. Calc. 40.20.

To 70 g of the alcohol in double the amount of ether at 25°, 53 g of 79% acetyl hydroperoxide was added. After 3 days the reaction products were treated as described in the previous experiment. The ether solution was dried by $MgSO_4$ and, after removal of the ether, the oxidation products were distilled under vacuum. The yield was 59 g of the epoxy alcohol with b. p. 50-52.5° (4 mm); the greatest part boiled at 51.5° (4 mm). It is a colorless, mobile liquid, with an odor of tertiary alcohols. It is soluble in cold water and organic solvents, rapidly decolorizes 1% $KMnO_4$ solution, displaces iodine from potassium iodide in aqueous solution, and contains active hydrogen.

n_D^{20} 1.4301, d_4^{20} 0.9288, MR_D 40.06; Calc. 40.24. γ^{20} 27.84. Found: P 354.3. Calculated: P 352.3 (by Sugden's Method)*

Found %: C 66.81; H 11.03; OH 10.14. M 150.7. $C_8H_{16}O_2$. Calculated %: C 66.66; H 11.11; OH 11.80. M 144.

Reaction of 2, 4-dimethyl-oxido-2, 3-hexanol-4 with zinc chloride. 1.0 g of powdered anhydrous $ZnCl_2$ was added to 5 g of the alcohol epoxide. The mixture became hot, and the liquid portion turned turbid. When heated on a water bath the liquid boiled and became clear. Water to dissolve $ZnCl_2$, and potash to salt out the reaction products were added to the reaction mixture, and the products were then extracted by ether and dried by $MgSO_4$. During the distillation of the reaction products the first 8 drops were collected in dimedone solution, in which crystals with m. p. 150-151° were formed after heating 2 hours on the boiling water bath, corresponding to the addition product of dimedone and isobutyraldehyde. The substance collected at b. p. 73-80° had the odor of methyl ethyl ketone.

n_D^{20} 1.3725, d_4^{20} 0.7972, MR_D 20.55; Calc. 20.68.

The semicarbazone (from ethanol) melted at 138-139°. A sample mixed with methyl ethyl ketone semicarbazone showed no depression of melting point.

Decomposition of 2, 4-dimethyl-oxido-2, 3-hexanol-4 in sulfuric acid solution. 10 g of the alcohol epoxide was added to 20 ml of water containing 0.2 g of H_2SO_4. The mixture was heated for 3 hours on the boiling water bath. At the end of the heating an odor of isobutyradehyde was detected in the flask; the sulfuric acid was neutralized by potash, while the reaction products were extracted with ether, dried by $MgSO_4$, and the volatile portion distilled off under normal pressure. The first portion was collected in dimedone solution, which gave an addition product with m. p. 148-149°, corresponding to isobutyraldehyde. The fraction boiling at 68-77° was collected in semicarbazide solution. A semicarbazone with m. p. 138-140° was formed. A sample mixed with methyl ethyl ketone semicarbazone gave no melting point depression.

* The parachor for the oxide ring and oxide oxygen was taken as 27 [63], and for hydroxyl as 13.3 [64].

The residue after distillation of the readily volatile products was distilled under vacuum. A substance with b. p. 78-80° (3 mm) was obtained. This is a liquid containing active hydrogen, which slowly displaces iodine from potassium iodide in aqueous solution and does not form a semicarbazone. In a hydrochloric acid solution of 2, 4-dinitrophenylhydrazine it gave a mixture of 2, 4-dinitrophenylhydrazones. One of these melted at 174-175°. A sample mixed with isobutyraldehyde of 2, 4-dinitrophenylhydrazone gave no melting point depression. The substance did not decompose when boiled with acidified water. Its analysis corresponded to the formula $C_8H_{16}O_2$. It has a considerably higher molecular weight than the original alcohol epoxide.

n_D^{20} 1.4482, d_4^{20} 0.9585

Found %: C 66.79; H 11.32; OH 12.39. M 185.2, 198.9. $C_8H_{16}O_2$. Calculated %: C 66.66; H 11.11; OH 11.80. M 144.

2, 4-Dimethyl-Oxido-2, 3-Heptanol-4 (I, R = C_3H_7)

Preparation. The epoxy alcohol was prepared by the oxidation of 2, 4-dimethylheptene-2-ol-4, which was synthesized from mesityl oxide and propylmagnesium bromide.

B. p. 70-72° (13 mm), n_D^{20} 1.4453, d_4^{20} 0.8521, MR_D 44.27; Calc. 44.82.

To 59 g of the alcohol in 120 ml of ether at 20-25° 44 g of 76% acetyl hydroperoxide was added. The reaction products were treated as before. Distillation yielded 39 g of a substance with b. p. 62-63° (4 mm). This was a mobile, colorless liquid with a pleasant odor. The substance contains active hydrogen, is easily oxidized by 1% K MnO_4 solution, and displaces iodine from potassium iodide in aqueous solution.

n_D^{20} 1.4317, d_4^{20} 0.9154, MR_D 44.74; Calc. 44.86. γ^{20} 27.40. Found P 394.9; Calc. P 391.3 (by Sugden's Method).*

Found %: C 67.96; H 11.62; OH 11.43. M 165.8, 166.5. $C_9H_{18}O_2$. Calculated %: C 68.35; H 11.39; OH 10.76. M 158.

Reaction of 2, 4-dimethyl-oxido-2, 3-heptanol-4 with zinc chloride. To 4.5 g of the epoxy alcohol 0.8 g of fused zinc chloride was added. Some heat evolution and turbidity was observed. When heated on the water bath to 85-90° the liquid boiled and became quite clear. An odor of isobutyraldehyde was given off. The reaction products were treated as previously. During the distillation the first portions were collected in dimedone solution, to give the crystalline addition product with isobutyraldehyde with m. p. 148-149°. The higher-boiling fractions yielded a substance with b. p. 100-102° (734 mm), which corresponded to methyl propyl ketone.

n_D^{20} 1.3930, d_4^{20} 0.8097, MR_D 25.35; Calc. 25.30.

The semicarbazone melted at 108-109°, and the 2, 4-dinitrophenylhydrazone at 141° [65].

Decomposition of 2, 4-dimethyl-oxido-2, 3-heptanol-4 in sulfuric acid solution. 18 g of the alcohol epoxide was added to 30 ml of water containing 0.3 g of H_2SO_4. After the mixture was heated on the water bath and then boiled, an odor of isobutyraldehyde was noted. The reaction products were treated as in the previous experiments. During the distillation the first runnings were collected in dimedone solution, where crystals with m. p. 148-149° were formed, indicating the presence of isobutyraldehyde. The residue was distilled under vacuum. The substance collected at b. p. 35-38° (63 mm) proved to be methyl propyl ketone. The semicarbazone melted at 108°.

From the higher boiling fractions a small amount of a substance with b. p. 92-94° (5 mm) was obtained. Its analysis almost agreed with the formula $C_9H_{18}O_2$.

* The parachor for oxide oxygen and the oxide ring, as before, was taken as 27.

n_D^{20} 1.4438, d_4^{20} 0.9353.

Found %: C 69.88; H 11.61. $C_9H_{18}O_2$. Calculated %: C 68.35; H 11.53.

Repeated distillations resulted in alteration of the substance and an increase of the percentage content of carbon.

2, 4-Dimethyl-Oxido-2, 3-Octanol-4 (I, R = C_4H_9)

Preparation. The alcohol epoxide was prepared by the oxidation of 2, 4-dimethyloctene-2-ol-4, which was synthesized from butylmagnesium bromide and mesityl oxide.

B. p. 60° (2.5 mm), n_D^{20} 1.4505, d_4^{20} 0.8546, MR_D 49.10; Calc. 49.44.

To 140 g of the alcohol in 200 ml of ether 74 g of 92.9% acetyl hydroperoxide was added. After 4 days the reaction products were treated as in the previous experiments. Distillation under vacuum gave 124 g of a substance with b. p. 76-77° (4 mm). This was a colorless mobile liquid with a pleasant odor. The substance is sparingly soluble in water and readily in organic solvents, is oxidized by 1% $KMnO_4$ solution, displaces iodine from potassium iodide in aqueous solution, and contains active hydrogen.

n_D^{20} 1.4344, d_4^{20} 0.9059, MR_D 49.48; Calc. 49.48.

Found %: C 69.55; H 11.77; OH 10.73. M 172.6. $C_{10}H_{20}O_2$. Calculated %: C 69.76; H 11.62; OH 9.88 M 172.

Decomposition of 2, 4-dimethyl-oxido-2, 3-octanol-4 in sulfuric acid solution. 8 g of the alcohol epoxide was added to 20 ml of water containing 0.2 g of H_2SO_4. An odor of isobutyraldehyde was noted after the mixture was shaken for several minutes. The mixture was heated about 1 hour on the boiling water bath. The volatile products were collected in dimedone solution, in which crystals with m. p. 148-149° were formed after twenty-four hours. The remaining reaction products were treated as in the previous experiments. Distillation yielded a substance with b. p. 127-129° (741 mm), which corresponded to methyl n-butyl ketone.

n_D^{20} 1.3991, d_4^{20} 0.8149, MR_D 29.69; Calc. 29.92.

The semicarbazone melted at 120-121° [65].

A substance with b.p. 115-116° (6 mm) was isolated from the higher-boiling fractions. This was an oily liquid which did not decompose when heated with water containing a few drops of sulfuric acid, did not liberate iodine from potassium iodide, did not form a semicarbazone, and contained active hydrogen. Analysis of this substance gave results close to the formula $C_{10}H_{20}O_2$.

n_D^{20} 1.4488, d_4^{20} 0.9393.

Found %: C 69.61; H 11.81; OH 7.23. M 207.6, 215.5. $C_{10}H_{20}O_2$. Calculated %: C 69.76; H 11.62; OH 9.94, M. 172.

Reaction of 2, 4-dimethyl-oxido-2, 3-octanol-4 with zinc chloride. 1.0 g of powdered fused zinc chloride was added to 10.8 g of the alcohol epoxide. When heated on the water bath to 75-80° the liquid boiled, and an odor of isobutyraldehyde was noted. The reaction products were treated as in the previous experiments. During the distillation the fraction boiling in the range 47-80° was collected in dimedone solution, in which a crystalline addition product with m. p. 149-150° was formed, which corresponded to the isobutyraldehyde adduct. The second fraction with b. p. 127-130° (735 mm) contained methyl n-butyl ketone. The semicarbazone melted at 120-121°.

During distillation of the higher boiling products under vacuum, about 1.0 g of a substance with b. p. 114-119° (6 mm) was obtained, which was not investigated.

The heating of 2, 4-dimethyl-oxido-2, 3-octanol-4 with water containing NaOH. 7 drops of 33% NaOH followed by 5.0 g of the alcohol epoxide was added to 20 ml of H_2O. The mixture stood twenty-four hours at room temperature, and was then heated 2-2.5 hours on the boiling water bath. There was no odor of isobutyraldehyde. The reaction products were extracted with ether, dried by $MgSO_4$ and distilled under vacuum. 4.0 g of a substance which proved to be the original alcohol epoxide was obtained.

B. p. 89.5° (11 mm), n_D^{20} 1.4340, d_4^{20} 0.9059, MR_D 49.44; Calc. 49.48.

The heating of 2, 4-dimethyl-oxido-2, 3-octanol-4 with diethylamine. 5.5 g of the alcohol epoxide and 6.0 g of diethylamine were sealed in a glass tube, and heated first on the boiling water bath, and then 6 hours in a tubular furnace at 135-140°. No excess pressure was observed when the tubes were opened. The diethylamine was driven off under vacuum, and the residue, which distilled completely at 80-80.5° (8 mm), proved to be the original alcohol epoxide.

n_D^{20} 1.4339, d_4^{20} 0.9047, MR_D 49.50; Cal. 49.48.

2, 4, 7-Trimethyl-Oxido-2, 3-Octanol-4 (I, R = iso-C_5H_{11})

Preparation. The epoxy alcohol was prepared by the oxidation of 2, 4, 7-trimethyloctene-2-ol-4 which was synthesized from isoamylmagnesium bromide and mesityl oxide.

B. p. 65° (1 mm), n_D^{20} 1.4488, d_4^{20} 0.8427, MR_D 54.01; Calc. 54.05.

To 150 g of the alcohol in 200 ml of ether 70 g of 93% acetyl hydroperoxide was added. After 3 days the reaction products were treated in the usual way. Vacuum distillation yielded 116 g of a substance with b. p. 71-72° (3 mm). This was a colorless mobile liquid, containing active hydrogen, which liberates iodine from potassium iodide in aqueous solution.

n_D^{20} 1.4340, d_4^{20} 0.8967, MR_D 54.02; Calc. 54.09.

Found %: C 71.14; H 12.09. M 183.3. $C_{11}H_{22}O_2$. Calculated %: C 70.97; H 11.82. M 186.

Decomposition of 2, 4, 7-trimethyl-oxido-2, 3-octanol-4 in sulfuric acid solution. 12 g of the alcohol epoxide was added to 20 ml of water containing 0.2 g of H_2SO_4. After the mixture was heated on the water bath an odor of isobutyraldehyde was noted. The reaction products were treated in the usual manner. The volatile decomposition products were distilled at normal pressure and collected in dimedone solution. A crystalline addition product with m. p. 149-150° was obtained. The residue was distilled under vacuum; 2 fractions were collected: the first at b. p. 28-97° (2 mm) and the second at 100-102° (2 mm). From the first fraction a substance with b. p. 144-145° (742 mm) was isolated.

n_D^{20} 1.4073, d_4^{20} 0.8172, MR_D 34.35; Calc. 34.54.

The semicarbazone of this substance melted at 142-143°. These data indicate the presence of methyl isoamyl ketone [65].

Analysis of the substance with b. p. 100-102° (2 mm) corresponded to the formula $C_{11}H_{22}O_2$.

n_D^{20} 1.4489, d_4^{20} 0.9191, MR_D 54.27; Calc. 54.53.

Found %: C 70.83; H 11.99; OH 8.57. $C_{11}H_{22}O_2$. Calculated %: C 70.97; H 11.82; OH 9.14.

On the assumption that this substance was an α-ketol, an isomerization product of the alcohol epoxide, we attempted to obtain a glycol from it by the reaction with phenylmagnesium bromide. The attempt was not successful.

SUMMARY

1. Five unsaturated tertiary alcohols were oxidized by acetyl hydroperoxide: 2, 4-dimethylpenten-2-ol-4, 2, 4-dimethylhexen-2-ol-4, 2, 4-dimethylhepten-2-ol-4, 2, 4-dimethylocten-2-ol-4, and 2, 4, 7-trimethyl-octen-2-ol-4, and 5 α, β-epoxy alcohols were prepared: 2, 4-dimethyl-oxido-2, 3-pentanol-4, 2, 4-dimethyl-oxido-2, 3-hexanol-4, 2, 4-dimethyl-oxido-2, 3-heptanol-4, 2, 4-dimethyl-oxido-2, 3-octanol-4, and 2, 4, 7-trimethyl-oxido-2, 3-octanol-4.

2. All the above alcohol epoxides decompose into isobutyradehyde and the corresponding ketones upon reaction with anhydrous zinc chloride, and also when heated with aqueous acid solutions.

3. A mechanism for the decomposition of α, β-epoxy alcohols is proposed on the basis of the possible enolization of the three-membered oxide ring.

4. Isomeric conversion of α-oxides into enols is apparently the reason for the discrepancy between the chemical properties of α-oxides and their cyclic structure.

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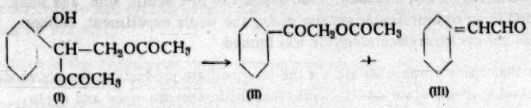
THE FORMATION OF ω-ACETOXYHEXAHYDROACETOPHENONE AND CYCLOHEXYLIDENEACETALDEHYDE FROM 1, 1-PENTAMETHYLENEGLYCEROL 2, 3-DIACETATE

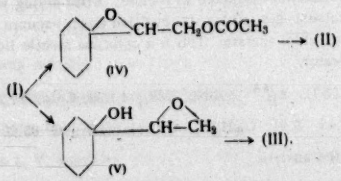
A. Ya. Berlin and L. V. Sokolova

As was already reported earlier [1] when 1, 1-pentamethyleneglycerol 2, 3-diacetate (I) is heated in boiling xylene in the presence of zinc dust, that is, the conditions of the so-called Serini reaction which is used for a number of steroid compounds, ω-acetoxyhexahydroacetophenone (II) is formed, in addition to a small amount of cyclohexylideneacetaldehyde (III):



There are no completely reliable data on the Serini reaction in the literature, and not one of the views put forward has been fully confirmed experimentally. However, L. Fieser and Huang-Minlon [2], L. Fieser and M. Fieser [3], and Shoppee [4] consider the most probable mechanism to be one associated with the intermediate formation of α-oxides.

In the present instance the transformations of 1, 1-pentamethyleneglycerol 2, 3-diacetate (I) may be represented as follows in agreement with this point of view:



The present study was undertaken for the experimental verification of this view.

The supposed intermediate product in the formation of ω-acetoxyhexahydroacetophenone (II), the acetate of 3, 3-pentamethyleneglycidol (IV), was prepared by acetylation of the corresponding alcohol epoxide, 3, 3-pentamethyleneglycidol [5] by means of acetic anhydride in pyridine at room temperature in 88.1 % yield. After the 3, 3-pentamethyleneglycidol acetate had been boiled 3 hours in xylene with zinc dust the original α-oxide (IV) was obtained unchanged, in a yield of 91.7 % of the amount taken for the reaction. An attempt to identify ω-acetoxyhexahydroacetophenone as the semicarbazone was not successful. Investigation of the xylene distillate obtained in the course of this reaction showed a complete absence of acetic acid, which was always partially distilled off with xylene in the experiments with 1, 1-pentamethyleneglycerol 2, 3-diacetate [1].

Bearing this in mind, and also taking into account the known fact that α-oxides are capable of rearrangement into the corresponding ketones under the action of acids, the experiment was repeated in the conditions described above, but with the difference that an equimolecular amount of acetic acid was gradually added to the reaction mixture during the entire reaction. However, here again the original α-oxide (IV) was obtained back in 90-92% yield, and no ω-acetoxyhexahydroacetophenone could again be found in the reaction products.

From these experiments it follows that the acetate of 3, 3-pentamethyleneglycidol, is not an intermediate product in the formation of ω-acetoxyhexahydroacetophenone from 1, 1-pentamethyleneglycerol 2, 3-diacetate.

As regards the simultaneous formation of cyclohexylideneacetaldehyde (III) in this reaction, it seemed reasonable to believe that, as was indicated above, in the present instance the intermediate product could be an α-oxide, namely 1, 1-pentamethyleneglycidol (V). If this assumption was correct, then cyclohexylideneacetaldehyde or its reduction product, cyclohexylacetaldehyde, should be formed when 1, 1-pentamethyleneglycidol is heated with zinc dust in xylene at the boiling point of the latter. However, experiments showed that both in the absence of free acetic acid, and when the latter was gradually added in an equimolecular amount during the whole experiment, neither cyclohexylideneacetaldehyde nor cyclohexylacetaldehyde was formed.

Thus, the results show that epoxy compounds are not the intermediate products in the conversion of 1, 1-pentamethyleneglycerol 2, 3-diacetate into ω-acetoxyhexahydroacetophenone and cyclohexylideneacetaldehyde.

The possibility is not excluded that these reactions occur with the intermediate formation of biradicals, since such a viewpoint is considered possible [6] for many reactions of a similar type, and in particular in an examination of the mechanism of the pinacoline rearrangement.

EXPERIMENTAL

3, 3-Pentamethyleneglycidol acetate (IV). To a solution of 9.77 g of 3, 3-pentamethyleneglycidol [5] in 100 ml of anhydrous pyridine, 7.72 g (10 % excess) of acetic anhydride in anhydrous pyridine was added drop by drop. The acetylation was continued 14 hours at room temperature. The reaction mixture was poured into 2 liters of water, and the solution extracted with ether. After drying with calcined magnesium sulfate and removal of the solvent, the residue was distilled under vacuum. The yield was 11.15 g (88.1%) of 3, 3-pentamethyleneglycidol acetate. This is a colorless mobile liquid, soluble in the usual organic solvents, insoluble in water.

B. p. 115-116° (10 mm), $d_4^{18.5}$ 1.0571, $n_D^{18.5}$ 1.4620, MR_D 47.90, Calc. 47.28.

Found %: C 65.04, 65.48; H 8.43, 8.91. $C_{10}H_{16}O_3$. Calculated %: C 65.20; H 8.74.

No mobile hydrogen was found in the analysis.

Treatment of 3, 3-pentamethyleneglycidol acetate in the conditions for the preparation of ω-acetoxyhexahydroacetophenone from 1, 1-pentamethyleneglycerol 2, 3-diacetate [1]. A solution of 8.5 g of 3, 3-pentamethyleneglycidol acetate in 500 ml of anhydrous xylene was boiled 3 hours with 85 g of activated zinc dust. Titration of the xylene distillate by 0.1 NaOH solution showed a complete absence of acetic acid.

After the usual treatment the product was distilled under vacuum, when 7.8 g of the original 3, 3-pentamethyleneglycidol acetate with b. p. 115-116° (10 mm), or 91.7 % of the amount taken for the reaction, was obtained. The residue in the flask was 0.4 g of resin. No crystalline semicarbazone was formed when an alcoholic solution of semicarbazide was added to the substance formed.

The experiment was repeated in the same conditions, but a solution of the equimolecular amount of glacial acetic acid in anhydrous xylene was added to the mixture during the entire reaction. Titration of the xylene distillate by 0.1 N NaOH solution showed 14.6 of the acetic acid taken. After the usual treatment of the reaction mixture and removal of the xylene, the original 3, 3-pentamethyleneglycidol diacetate, with b. p. 114.5-116° (10 mm) was obtained in 92% yield. A crystalline semicarbazone again could not be obtained.

Treatment of 1, 1-pentamethyleneglycidol in the conditions for the formation of cyclohexylideneacetaldehyde from 1, 1-pentamethyleneglycerol 2, 3-diacetate [1]. A solution of 10 g of 1, 1-pentamethyleneglycidol [5] in 600 mo of anhydrous xylene was boiled 4 hours with 100 g of activated zinc dust. The xylene which was distilled off in small portions was turbid. After the usual treatment the substance was distilled at 10 mm. The following fractions were obtained: first 60-72°, yellowish color; second 74-75°, yellow color; third 90-95°, colorless liquid. Not one of these fractions gave the Schiff's reaction characteristic for aldehydes. The third fraction was 50% of the total weight of the fractions, and consisted of the original 1, 1-pentamethyleneglycidol. The first fraction mainly consisted of xylene. After additional fractionation of the first and second fractions, several drops of a yellow liquid, b. p. 75° (10 mm) were obtained.

Found %: C 73.86, 73.66; H 11.90, 12.02; H 0.83, 0.84.

The action of an alcoholic solution of semicarbazide on this substance gave 15 g of a semicarbazone with m. p. 183-185° (corr.) which gave a melting point depression with the semicarbazones of cyclohexylideneacetaldehyde and cyclohexylacetaldehyde. This substance was not studied further owing to the small quantity available.

A repetition of the experiment in the same conditions, but with the addition of an equimolecular amount of acetic acid during the entire reaction, also did not give a positive result: neither cyclohexylideneacetaldehyde, nor cyclohexylacetaldehyde could be found in the reaction products.

SUMMARY

1. It was shown that 3, 3-pentamethyleneglycidol acetate is not an intermediate product in the conversion of 1, 1-pentamethyleneglycerol 2, 3-diacetate into ω-acetoxyhexahydroacetophenone.

2. It was shown that 1, 1-pentamethyleneglycidol is not an intermediate reaction product in the conversion of 1, 1-pentamethyleneglycerol 2, 3-diacetate into cyclohexylideneacetaldehyde and into cyclohexylacetaldehyde.

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* T. p. = C. B. translation pagination.

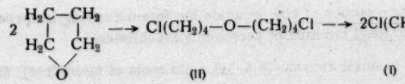
OPENING OF THE FURANIDINE RING BY MEANS OF ACID CHLORIDES

V. I. Lutkova, N. I. Kutsenko and M. I. Itkina

According to the literature, opening of the furanidine ring with the formation of dihalogen compounds of the aliphatic series has been effected by means of hydrochloric acid, phosphorus oxychloride, thionyl chloride and other acid chlorides. In most of the papers it is reported that the main reaction product is 1, 4-dichlorobutane, with 4, 4'-dichlorodibutyl ether as a side product.

The action of hydrogen chloride, sulfuric acid and water at 180° under a pressure of 20 atmospheres on furanidine gives 1, 4-dichlorobutane and some 1, 4-dichlorodibutyl ether [1]. Smorgonsky and Goldfarb obtained 1, 4-dichlorobutane by the reaction of furanidine with thionyl chloride in the presence of zinc chloride. They also obtained 1, 4-dichlorobutane by the reaction between furanidine and gaseous hydrogen chloride in the presence of $SnCl_2$ [2]. Opening of the furanidine ring with the formation of 1, 4-dichlorobutane was effected by hydrogen chloride in the presence of $ZnCl_2$ (up to 50 % of the weight of furanidine) [3], and by hydrogen chloride in the liquid or gas phase at 60-200° in the presence of heterocyclic amines or quaternary ammonium bases [4]. When furanidine and hydrogen chloride vapors were passed through a reactor filled with Al (95%) and anhydrous $AlCl_3$ (5%) at 215°, 1,4-dichlorobutane was obtained [5]. When the furanidine ring was opened by phosphorus oxychloride in the presence of sulfuric acid, the main reaction product was 4, 4'-dichlorodibutyl ether [6].

The present study was performed in order to elucidate the reaction mechanism and to establish the conditions for the opening of the furanidine ring. Opening of the ring was effected by phosphorus oxychloride and thionyl chloride. When the reaction was carried out both with phosphorus oxychloride and with thionyl chloride it was established that, according to the conditions of the experiment, the reaction could be directed toward formation either of 1, 4-dichlorobutane or of 4, 4'-dichlorodibutyl ether. The direction of the reaction is influenced by the amount of anhydrous zinc chloride used as catalyst. Additions of small amounts of zinc chloride (0.5-1.0 g per mole of furanidine) lead to the formation of 4, 4'-dichlorodibutyl ether as the main product. When zinc chloride up to 10% of the weight of the furanidine is added, the main product is 1, 4-dichlorobutane (I) and 4, 4'-dichlorodibutyl ether (II) is formed as a side product. It was established that 4, 4'-dichlorodibutyl ether is the intermediate product in the preparation of 1,4-dichlorobutane:



(II) (I)

EXPERIMENTAL

Opening of the furanidine ring by means of thionyl chloride. 72 g of furanidine (b. p. 64-66°, d_4^{20} 0.888, n_D^{20} 1.4074) and 1 g of anhydrous zinc chloride was placed in a four-necked flask with a reflux condenser, stirrer, thermometer, and dropping funnel, 119 g of thionyl chloride was added at 60° from the dropping funnel, and the mixture was heated at 120° until evolution of SO_2 ceased. At the end of the reaction the contents of the flask were poured out into a saturated solution of common salt, the reaction product was separated off, washed with water, dried by sodium sulfate, and distilled. The first fraction, collected at 48-50° (13 mm) contained 1, 4-dichlorobutane in a yield of 21.6 g (17%), and the second fraction, which distilled at 126-128° (13 mm), contained 4, 4'-dichlorodibutyl ether in a yield of 64 g (64.3%).

When the amount of zinc chloride added was up to 10% of the furanidine, it was possible to direct the reaction toward preferential formation of 1, 4-dichlorobutane, namely: 1 mole of furanidine gave 90 g (71.0%) of 1, 4-dichlorobutane and 8.3 g (14.2%) of 4, 4' dichlorodibutyl ether.

1,4-Dichlorobutane: b. p. 48-50° (13 mm), d_4^{20} 1.1280, n_D^{20} 1.4520, MR_D 30.37; Calc. 30.40.

Found %: C 38.24; H 6.28; Cl 55.38. $C_4H_8Cl_2$. Calculated %: C 38.10; H 6.30; Cl 55.55.

4,4'-Dichlorodibutyl ether: b. p. 126-128° (13 mm), d_4^{20} 1.0810, n_4^{20} 1.4568, MR_D 50.11; Calc. 50.52.

Found %: C 47.68; H 8.47; Cl 35.50. $C_8H_{16}OCl_2$. Calculated %: C 47.70; H 7.80; Cl 35.69.

Opening of the furanidine ring by means of phosphorus oxychloride. 102 g of phosphorus oxychloride and 12 g of anhydrous zinc chloride were placed in a round-bottomed flask fitted with a stirrer, thermometer, reflux condenser and a dropping funnel, and 72 g of furanidine was added at 60-70° from the dropping funnel. The mixture was heated to 100-107° and then cooled, and 75 ml of water was added to decompose the additional compound formed. When evolution of hydrogen chloride stopped, the reaction product was separated from the acid solution, washed with common salt solution, then with water, dried and distilled.

Two fractions were obtained: first, b. p. 48-50° (13 mm), in 75.6 g (60%) yield, which was 1,4-dichlorobutane, and the second, b. p. 126-128° (13 mm), in 6.9 g (7%) yield, which was 4,4'-dichlorodibutyl ether. When the amount of zinc chloride added was 0.5 g per mole of furanidine, 4, 4'-dichlorodibutyl ether in 52.7 g (55%) yield, and 1, 4-dichlorobutane in 16.3 g (12%) yield were obtained. The products fully agreed in their analytical constants with the data given above.

Elucidation of the reaction mechanism. It was assumed that 4, 4'-dichlorodibutyl ether is the intermediate reaction product in the formation of 1, 4-dichlorobutane. To confirm this a series of experiments was carried out on the preparation of 1, 4-dichlorobutane from 4, 4'-dichlorodibutyl ether. The experiments were carried out in the same conditions as in the preparation of 1, 4-dichlorobutane from furanidine, but instead of the latter the corresponding amount of 4, 4'-dichlorodibutyl ether was used. 75 g of 4, 4'-dichlorodibutyl ether gave 55 g (57.5%) of 1,4-dichlorobutane, while the unreacted 4,4'-dichlorodibutyl ether was obtained unchanged.

SUMMARY

1. It was established that in the presence of zinc chloride the furanidine ring is opened without increase of pressure by the action of thionyl chloride or phosphorus oxychloride.

2. When zinc chloride is used in small amounts (0.5-1.0 g per mole of furanidine), the main reaction product is 4, 4'-dichlorodibutyl ether.

When the amount of zinc chloride is up to 10% of the weight of the furanidine, 1, 4-dichlorobutane is the main product.

3. It was shown that 4, 4'-dichlorodibutyl ether is the intermediate product in the formation of 1,4-dichlorobutane from furanidine.

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THE REACTION BETWEEN VINYL ESTERS AND PRIMARY AROMATIC AMINES

N. S. Kozlov and I. A. Shur

Many different methods for the synthesis of quinoline derivatives have now been developed, with primary aromatic amines and various organic compounds – glycerol, aldehydes, ketones, ketonic acids, diketones, acetylene, etc. – as starting materials.

Recently a paper was published by Poral-Koshits [1] in which a method for the preparation of quinaldine from aniline and vinyl ethers is described. There is no doubt that in the experimental conditions used vinyl-ethers [2] are hydrolyzed with the formation of acetaldehyde [3], which then reacts with aniline to form quinoline bases.

In this connection a study of the reaction between vinyl esters and primary aromatic amines would be of great interest.

The literature contains an indication [4] that primary aromatic amines can be acylated with the aid of vinyl esters. Thus, benzanilide was obtained by the reaction of aniline with vinyl benzoate, and butyranilide by the reaction with vinyl butyrate.

On the basis of the properties of esters it was presumed that if the reaction was carried out in an aqueous solution of a mineral acid, the reaction might be expected to take another direction. The explanation is that in an acid medium hydrolysis of vinyl esters results in the formation of acetaldehyde, which may subsequently react with the primary amines. We established that quinoline bases are formed by the reaction of primary aromatic amines with vinyl esters in an acid medium. Aniline gave rise to quinaldine, and aniline homologs yielded the corresponding quinaldine homologs. In these reactions vinyl butyrate may be replaced by vinyl acetate and apparently also by other vinyl esters. The yield of the quinoline base is increased if the vinyl ester is introduced in larger molar proportions.

EXPERIMENTAL

Experiment 1. 7.5 g (0.065 mole) of vinyl butyrate was added dropwise to a reaction mass consisting of 6 g (0.065 mole) of aniline and 10 ml of concentrated hydrochloric acid heated on a water bath in a round-bottomed flask with a reflux condenser. The reaction was completed in 2 hours. The reaction mass was cooled and treated with a solution of alkali, the reaction products were extracted with ether, and the residue after removal of the latter was distilled. The substances in the fraction which boiled at 190-260°, which totalled 6 g, were completely soluble in hydrochloric acid; they were converted into the picrate. After recrystallization from alcohol the picrate melted at 191° (yield 6 g). A sample mixed with quinaldine picrate gave no melting point depression. The yield of quinaldine was 40.5% (calculated on the aniline taken for the reaction). After neutralization of the alkaline solution 2 g of butyric acid was isolated.

Experiment 2. The reaction between 6 g of p-toluidine (0.056 mole), 10 ml of concentrated hydrochloric acid, and 6.4 g of vinyl butyrate (0.056 mole) was carried out under the same conditions.

The quinoline base, containing in 6 g of the fraction which boiled at 205-270°, were converted into the picrate; after recrystallization from alcohol it melted at 191°, yield 6.5 g. A sample mixed with 2, 6-dimethylquinoline picrate gave no melting point depression. Decomposition of the picrate gave 2, 6-dimethylquinoline with m. p. 60°. The yield of the quinoline base was 29.48% (on the p-toluidine taken for the reaction). 2 g of butyric acid was isolated from the alkaline solution.

Experiment 3. 6 g of m-toluidine, 10 ml of concentrated hydrochloric acid and 6.4 g of vinyl butyrate was taken for the reaction. The reaction was carried out as in the preceding experiment. 7 g of the quinoline base contained in the fraction boiling at 205-265° was converted into the picrate; after recrystallization from alcohol this melted at 189°, yield 7 g. A sample of the picrate mixed with 2, 7-dimethylquinoline picrate gave no melting point depression. Decomposition of the picrate gave 2, 7-dimethylquinoline with m. p. 62°. The yield of the quinoline base was 31.7% (on the m-toluidine taken for the reaction).

Experiment 4. 6 g of m-xylidine (0.0502 mole), 10 g of concentrated hydrochloric acid, and 5.7 g of vinyl butyrate (0.050 mole) was taken for the reaction.

5.5 g of the fraction which boiled at 220-280° gave 6 g of a picrate with m. p. 190°. A sample mixed with 2, 6, 8-trimethylquinoline picrate gave no melting point depression. The yield of the quinoline base was 30.3% (on the m-xylidine taken for the reaction).

SUMMARY

The reaction between primary aromatic amines (aniline, p-toluidine, m-toluidine, and m-xylidine) and vinyl esters results in the formation of quinoline bases – quinaldine and its derivatives. This reaction may be regarded as a new method for the preparation of quinoline bases.

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ANHYDRIDES, AMINO AND GUANIDO DERIVATIVES OF HYDROCARBONS AND POLYHYDRIC ALCOHOLS

III. AMINATION AND GUANIDATION OF HYDROCARBONS *

S. N. Danilov and I. S. Lishansky

An earlier paper [1] dealt with amino, methylamino and guanido derivatives prepared from 5, 6-anhydroglucofuranose. In the present paper experiments are described on the synthesis of similar derivatives based on 2, 3-anhydro-4, 6-benzylidene-α-methyl alloside (III), which was prepared from 4, 6-benzylidene-α-methyl glucoside (I) through its 2, 3-ditosyl compound (II), when the formation of the α-epoxy ring was accompanied by a group rearrangement at the second carbon atom (allose was formed from glucose).

Various methods [2] are known for the introduction of amino groups into hydrocarbon and polyhydric alcohol molecules: 1) substitution of an amino group into halogen derivatives, 2) the same in tosyl (toluene sulfonic acid) or mesyl (methane sulfonic acid) derivatives, 3) through alpha-anhydro compounds. However, in the case of 5, 6-anhydroglucose the introduction of a guanido group could only be effected by the action of S-methylisothiourea and O-methylisourea on amino compounds [1].

The direct replacement of sulfonic, mesyl, and tosyl groups by ammonia and amino residues in monoses and cellulose is effected incompletely and with great difficulty.

The addition of ammonia and amines at the α-oxide ring in monoses and polyhydric alcohols takes place much more easily, but this, like the formation of the α-oxide groups themselves, is generally accompanied by a spatial regrouping (Walden inversion) of the secondary alcohol groups at one of the carbon atoms. In the case of 2, 3-anhydro derivatives of monoses it is possible even to add on guanidine in pyridine solution at the α-oxide ring. If the guanidation experiment is carried out in an alcoholic medium, a molecule of alcohol is added at the oxide ring, as in the presence of alcoholates or alcoholic alkali.

In this way, by the action of ammonia, methylamine, and guanidine respectively on 2, 3-anhydro-4, 6-benzylidene-α-methyl alloside, the following were isolated and identified: 2-desoxy-2-amino-4, 6-benzylidene-α-methyl altroside (IV), 2-desoxy-2-methylamino-4, 6-benzylidene-α-methyl altroside (V), and 2-desoxy-2-guanido-4, 6-benzylidene-α-methyl altroside (VI). There was again a regrouping at the second carbon atom, so that altrose was formed from allose.

It has already been mentioned that, as in the action of alcoholates on α-oxide derivatives, an alcohol molecule is added at the ring in the presence of guanidine: 2-methyl-4, 6-benzylidene-α-

* For the second paper in this series see S. N. Danilov and V. F. Kazimirova, J. Gen. Chem., Coll. II, 1946 (1953).

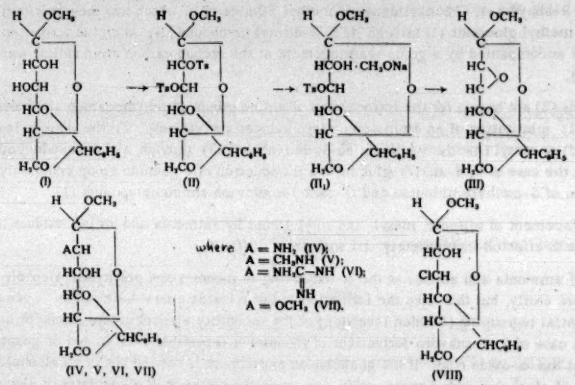
-methyl altroside (VII) was isolated from the reaction products.

The action of guanidine hydrochloride on 2, 3-anhydro-4, 6-benzylidene-α-methyl altroside gave 3-chloro-4, 6-benzylidene-α-methyl glucoside (VIII).

The characteristic displacement of the hydrogen atoms and substituent groups at the (2, 3) asymmetric carbon atoms in monoses on closure of the α-oxide ring is regarded in the literature [3] in terms of electrophilic (cationogenic) groups and trans-exchange of anionoid groups at the potential carbonium cation. The necessity for a trans-configuration in the formation of a 2, 3-anhydro ring by the action of sodium alcoholate may be explained [4] by the addition of the alcoholate to the free hydroxyl group (see Formula II). The alcoholate addition product formed then decomposes with formation of a sulfonate and an anhydro sugar; this is accompanied by inversion at the carbon atom where the tosyl group was previously present.

If the α-ring between the second and third carbon atoms in a monose is broken, the substituent may be attached to one or the other of the carbon atoms.

The action of ammonia or sodium methylate on a 2, 3-anhydro derivative of allose gives mainly altrose derivatives with the substituent at the second carbon atom, as in our experiments (Formulas IV-VII), while the action of hydrogen chloride on the 2, 3-anhydro ring gives a chloro derivative with the chlorine at the third carbon atom in glucose (Formula VII).



EXPERIMENTAL

1. Amination (guanidation) of 1, 2 – 5, 6-diisopropylidene-3-tosylglucofuranose, 1, 2 – 3, 4-diisopropylidene-6-tosylgalactose and cellulose mesyl esters.

a) Diisopropylideneglucose with m. p. 111-112° was obtained by a known method, as indicated previously [1]. The toluene sulfonate (tosyl) ester, 1, 2 – 5, 6-diisopropylidene-3-tosylglucofuranose, was synthesized as described in the literature by the action (12 hours at 30°) of toluene chlorosulfonate in dry pyridine, with 92% yield. After recrystallization from methyl alcohol the m. p. was 120-121°, which agrees with the literature data for 1, 2 – 5, 6-diisopropylidene-3-tosylglucofuranose [5].

For the introduction of a guanido instead of a tosyl group in the 3 position, this glucose derivative was heated 30 hours at the boil in alcoholic solution with guanidine. 4.1 g of the tosyl ester and 100 ml of

an alcoholic solution of guanidine, containing 1.18 g of the base, was taken. The tosyl ester reacted completely, as was confirmed by the absence of turbidity when a sample of the solution was diluted with water. Shiny, scaly crystals of guanidine p-toluene sulfonate (1.2 g) and of 1, 2 – 5, 6-diisopropylideneglucofuranose (1.8 g, 70% calculated on the tosyl ester taken). After recrystallization from ligroine the diisopropylideneglucose had m. p. 110-111°, and gave no melting point depression when mixed with known 1, 2 – 5, 6-diisopropylideneglucofuranose. The residue after extraction of the diisopropylideneglucose with ethyl ether gave no color with Sakagushi's reagent for the guanido group (a solution of 0.1 g of α-naphthol in 100 ml of 0.5 % caustic soda solution followed by the addition of 1% sodium hypochlorite solution produces a crimson color which vanishes in presence of excess hypochlorite).

No replacement of the tosyl group by a guanido group was found, but only hydrolysis of the former when tosylglucofuranose was heated 24 hours with guanidine in alcoholic solution in an autoclave at 140°. The residue after removal of the alcohol was extracted with chloroform; the product obtained after removal of the chloroform and recrystallization from ligroine had m. p. 110-111°, and was 1, 2 – 5, 6-diisopropylideneglucofuranose (yield about 70%).

b) The galactose derivative, 1, 2 – 3, 4-diisopropylidene-6-tosylgalactose, obtained as described in the literature [6], had m. p. 101-103°. After a solution of this tosyl ester (20 g) in dry methyl alcohol (250 ml) was heated with guanidine (10.5 g) at the boil for 38 hours, 6.4 g of tosyl ester and syrupy diisopropylideneglactose was obtained. Thus, in the case of the tosyl derivative of diisopropylidenegalactose also, hydrolysis and not substitution of the tosyl group took place.

c) Treatment of cellulose tosyl esters by ammonia, according to the literature results only in a low degree of replacement of the tosyl groups by amino groups.

In a search for a method for the amination of cellulose, both for a comparison of amino celluloses with chitin and because of the dyeability of aminated cellulose by acid dyes, we performed experiments on the replacement of methane sulfonic acid groups by amino groups in cellulose mesyl esters, which have been studied little. The mesyl groups in monoses, even at the second and third carbon atoms, react with sodium iodide, in contrast to tosyl esters, in which the tosyl group at the sixth carbon atom is usually easily substituted.

However, our experiments showed that the mesyl groups in cellulose are only weakly substituted by amino groups.

The acid chloride of methane sulfonic acid (CH_3SO_2Cl) was synthesized from thiosulfate by the action of dimethyl sulfate followed by chlorine in an aqueous medium. When the chlorination was performed at low temperatures (−10° to −18°) (to avoid hydrolysis of the acid chloride, which increases rapidly with rise of temperature) yields of up to 95% of the acid chloride were obtained (85% on the weight of the dimethyl sulfate consumed). The acid chloride had b. p. 159° (754 mm).

Before mesylation, the cellulose was activated either by treatment with 18% caustic soda solution at room temperature and on freezing, followed by removal of the alkali by washing, and drying; or in pyridine heated to the boil and with 3-fold freezing; or by grinding in a colloid mill. The cellulose was dehydrated by acetone and methyl alcohol, and then dried at 60°. The cellulose was put into pyridine and the methane sulfonic acid chloride was gradually added (at −10°, and at the end at + 20°). The fibrous mass which was filtered off (after 48 hours) had a yellow color. Analysis (for sulfuric acid after fusion of the cellulose mesyl ester with caustic potash or saltpeter) showed that esters [7] of the type $[C_6H_{10-x}O_{5-x}(OSO_2CH_3)_x]_n$, were obtained, the content (x) of mesyl groups in the molecules of which was 1.5 to 1.7 per glucose residue.

The mesyl esters do not dissolve or even swell in the usual organic solvents. They partly dissolve in boiling acetonylacetone. Phosphoric acid (80-85%) completely dissolves these esters in the cold, homogeneous solutions with an ester concentration up to 2.5% being possible. Esters with the former degree of esterification are precipitated from such solutions in the form of small flakes by water.

The degree of esterification was not increased when the mesylation was effected by means of methane sulfonic acid anhydride, prepared not only from the silver salt, as usual, but also from the lead salt of methane sulfonic acid and its acid chloride. The anhydride had m. p. 71°.

The cellulose mesyl esters were treated either 9 days with liquid ammonia (in sealed steel tubes) or 3 hours with gaseous ammonia at 130-140° in an autoclave or with solutions of ammonia in methyl alcohol or cellosolve at 100, 120-130, and 130-140° from 6 to 70 hours. The highest degrees of substitution were obtained by the action of alcoholic ammonia solutions at 130-140° during 40-70 hours, when the nitrogen content of the products reached 2.5-4.2%, while the sulfur content fell from 17-18 to 14-12%.

Trisubstituted sulfuric acid esters of cellulose, $[C_6H_7O_2(OSO_2OH)_3]_n$, obtained in the form of a colorless fibrous mass (by treatment of dried cellulose with a gaseous mixture of sulfur trioxide and nitrogen, or with solutions of sulfur trioxide in carbon disulfide and in dichloroethane) do not exchange sulfuric acid groups for ammonia residues. The action of liquid ammonia (−40°) resulted in the formation of water-soluble ammonium salts of cellulose sulfuric acid esters. Samples of cellulose partially oxidized by periodic acid to an iodine number 4-6 are readily aminated by virtue of their aldehyde groups, and the aminated fibers were satisfactorily dyed by wool dyes.

2. Synthesis of 2, 3-ditosyl-4, 6-benzylidene-α-methyl glucoside and 2, 3-anhydro-4, 6-benzylidene-α-methyl allosíde (III).

a) The starting α-methyl glucoside (m. p. 164-165°) was prepared as described in the literature [8], and 4, 6-benzylidene-α-methyl glucoside by Freudenberg's method [9] in the presence of freshly fused zinc chloride (yield up to 62%).

The benzylidene derivative of α-methyl glucoside was washed with benzene and with aqueous soda solution and recrystallized from hot water; m. p. 160-161°.

The ditosyl ester was prepared by the methods of Ohle [10] and Hudson [11] modified to decrease to consumption of pyridine (by 35 %), with the conditions for the decomposition of the reaction mixture chosen to ensure complete removal of pyridine, and with the product purified by recrystallization from acetone (and not from methyl alcohol as used by Ohle). 2, 3-ditosyl-4, 6-benzylidene-α-methyl glucoside was isolated in crystalline form in good yield (95-98 %).

It should be mentioned that p-toluene chlorosulfonic acid was obtained by purification of the technical product (by-product of the saccharine industry) by stirring it with soda solution on a boiling water bath (3-4 times repeated). The fused mass of chlorosulfonate was granulated by means of a strong jet of cold water. The moist product was dissolved in benzene on the water bath at 40-50°. After standing, drying, and filtration to remove suspended impurities, the solutions were cooled, and the crystals of toluene chlorosulfonic acid were separated off; after recrystallization from benzene the m. p. was 68-69°. The pyridine was dried over caustic potash.

45 g of benzylidene-α-methyl glucoside was dissolved in 200 ml of anhydrous pyridine, and 115 g of p-toluene chlorosulfonic acid, which dissolved instantly, was added. After 10 days of storage in a closed jar the whole volume of the liquid became filled with large crystals of the pyridine salt. Water was added dropwise, with stirring, till a permanent turbidity was formed; crystals were soon deposited copiously from the reaction mixture, which became heated. Finely chopped ice was added, and the contents of the jar were shaken on the machine, after which the grey powder was filtered off, treated with 3% hydrochloric acid with addition of ice, and the shaking was continued.

92 g of a substance (a steady yield of 94-98% of theoretical in the different experiments) was isolated; after recrystallization from hot acetone (colorless fine crystals) this had m. p. 148-149°, in agreement with the literature data.

b) The anhydride was obtained (in 90% yield) by a method which differed from that originally proposed by Robertson [12] (yield of anhydride 14%) and from Hudson's method [11] (yield 70%). The

conversion of the ditosyl ester into the anhydride by the action of sodium methylate in excess takes place in two stages, when first one tosyl group at the second carbon atom is hydrolyzed, and only after this a tosyl group (at the third carbon atom) and a hydroxyl hydrogen (at the second carbon atom) split off to form the α-oxide ring, with a spatial rearrangement taking place.

Robertson treated the ditosyl ester with a solution of sodium methylate in boiling methyl alcohol during 12 hours, and Hudson used a solution of sodium methylate in a mixture of methyl alcohol and dichloroethane at −10° during 3 days, followed by 2 more days at 20°, with continuous shaking during the first 2 days.

In order to find favorable conditions for synthesis of the anhydride, we carried out experiments with stirring at different temperatures and with different ratios of the ditosyl ester and sodium methylate. The rate of anhydride formation rises sharply with increase of temperature. The rate of decomposition of the anhydride formed by sodium methylate already becomes appreciable above 25°, with the formation of 2-methyl-4, 6-benzylidene-α-methyl altroside. It is necessary to have sodium methylate in excess over the two equivalents theoretically required, in order to increase the reaction rate and the yield of anhydride, but at a temperature below 25°. Vigorous stirring at the start of the synthesis is necessary to prevent the reaction mixture from separating into layers.

About 25 synthesis experiments were performed under different conditions at 20°, the yield varying from 30-94%. In some instances the yields were low owing to incomplete utilization of the tosyl ester and cleavage of the anhydride ring with addition of the alcohol.

We give a description of an experiment in the most favorable conditions. Purified 2, 3-ditosyl-4, 6-benzylidene- α-methyl glucoside (22.2 g) was dissolved in anhydrous dichloroethane in a 0.5 liter jar with a ground glass stopper.

A solution of sodium methylate was rapidly added (5.2 g of sodium in 100 ml of anhydrous methyl alcohol, which is three times the calculated amount of sodium methylate). The jar was shaken mechanically for 6 hours at room temperature and left 14 hours at the same temperature. The reaction mixture was then diluted by 200 ml of dichloroethane and washed with water in a separating funnel. The dichloroethane layer was separated off, the wash waters were extracted by dichloroethane, the dichloroethane solution was washed with water to a neutral reaction and dried over calcium chloride. The dichloroethane was distilled off under vacuum on a boiling water bath. The almost colorless product was washed with cold acetone. The yield was 1.0 g (94%), and after drying the product had m. p. 199-200°, which agrees with known data for 2, 3-anhydro-4, 6-benzylidene-α-methyl alloside.

No unreacted tosyl ester could be found in the acetone used for the washing. In successful syntheses there was neither any anhydride, nor the product of its decomposition by methyl alcohol, in the aqueous alcoholic layer separated off from the dichloroethane layer.

The experiments showed that:

1) the use of the theoretically required amount of sodium methylate results in the return of a considerable amount of the original tosyl ester (24-50%) and in a low yield of anhydride, but products of the cleavage of the anhydride ring are then absent;

2) excess of sodium methylate increases the yield of anhydride, the highest yields being obtained when the amount of the alcoholate is 3 times the theoretical;

3) increase of the reaction temperature above 25° leads to a sharp increase of the anhydride decomposition product (2-methyl-4, 6-benzylidene -α-methyl altroside) up to 50 % calculated on the tosyl ester taken.

In some experiments, because of cleavage of the α-anhydride ring by the alcohol, it was necessary to extract from the aqueous alcoholic layer a considerable amount of syrup which crystallized after seeding and prolonged keeping. The resultant crystals of 2-methyl-4, 6-benzylidene-α-methyl altroside had m. p. 98°. The same product was also obtained when 2, 3-anhydro-4, 6-benzylidene was heated with alcoholic guanidine solution, as will be described below.

3. 2-Desoxy-2-amino-4, 6-benzylidene-α-methyl altroside (IV)

The method described in the literature [13] for amination at 150° does not give good results, and we therefore used another method, with the experiments carried out in an autoclave made from stainless EYa-1-T steel, of 240 ml capacity. The autoclave was cooled to −15° and charged with dry 2, 3-anhydro-4, 6-benzlidene-α-methyl alloside and a solution of dry ammonia in anhydrous methyl alcohol saturated at −15° (150 ml of the alcohol containing 20 g of ammonia). The autoclave was heated 72 hours at 100°, cooled to 0°, and opened. The unreacted anhydride (2.5 g) was filtered off. The mother liquor was partly evaporated under vacuum, the crystals removed by filtration, and the evaporation repeated. However, as all the fractions contained the same product (m. p. 165-168°), in the subsequent experiments the liquid was evaporated to dryness in one stage. The powdered reaction product was washed with ethyl alcohol to remove colored impurities. After recrystallization from hot water, which removed residual anhydride, 12.1 g (91%) of a substance in the form of fine needles which formed a felted mass, with m. p. 168-169° was obtained. The literature gives m. p. 162-167° for a mixture of isomers with the amino group at the second and at the third carbon atoms.

Analysis confirmed the formula of the product as 2-amino-4, 6-benzylidene- α-methyl altroside.

Found %: N 5.10 (average of two). $C_{14}H_{19}O_5N$. Calculated %: N 4.97.

The substance is soluble in alcohol, acetone, and chloroform, and dissolves with difficulty in ether and in water. The alcoholic and particularly the acetone solution deposits fine crystals on rapid cooling, so that the solution resembles a gel which liquefies on warming. Aqueous and aqueous-alcoholic solutions of the amino derivative do not color phenolphthalein; they form salts with strong acids but not with carbonic acid. A cold 3% solution of dry hydrogen chloride was added dropwise to an acetone solution of the base cooled to +5° until a neutral reaction to methyl orange was obtained. The crystals of the salt which were deposited were removed by suction and washed with anhydrous acetone. They consisted of large fine white needles, easily soluble in water. After drying in vacuum at 70° over phosphoric anhydride the previously unknown hydrochloride had m. p. 129-130°.

To prepare the picrate, a cold saturated aqueous solution of picric acid was added to a dilute solution of the base. The precipitated picrate was recrystallized from hot aqueous 20% methyl alcohol, and was in the form of golden yellow small needles easily soluble in alcohol. After being dried in a vacuum at 100° over phosphoric anhydride the picrate had m. p. 161-162°, which was unchanged after another recrystallization of the product.

The ether solution obtained by the washing of the crude amino derivative contained a very small amount of what was apparently another isomer of the amino compound (with the amino group at the third carbon atom) which was detected as the picrate melting at 141-143°, a sample of which, mixed with the previously described picrate with m. p. 161-162°, gave a melting point depression.

The acetamide derivative of 2-desoxy-2-amino-4, 6-benzylidene -α-methyl altroside was obtained by the action of acetic anhydride in pyridine (2 g of the amine, 15 ml of pyridine, and 8 ml of acetic anhydride). After storage at 20° for 3 days the solution was diluted with 100 ml of chloroform, washed with water, 3% hydrochloric acid, bicarbonate solution, and again with water. The solution was dried over calcium chloride and evaporated under vacuum to a small volume (10 ml); the resultant syrup was placed in a crystallizing dish into a desiccator with sulfuric acid. The crystalline residue formed after drying had m. p. 181-182°. The literature [13] gives m. p. 184° for 2-acetamido-3-acetyl-4, 6-benzylidene- α-methyl altroside. It should be noted that the acetyl derivative of the other possible isomer of the amine has m. p. 270°.

This confirms that the amino sugar obtained has an amino group at the second carbon atom, and is 2-desoxy-2-amino-4, 6-benzylidene-α-methyl altroside.

The yield of the amino sugar varied from 59 to 91% in the different experiments.

The amino product formed was used for experiments on the synthesis of the guanido compound by the action of S-methylisothiourea and O-methylisourea.

A solution of S-methylisothiourea as the free base, or as the hydriodide or sulfate in the same solvents, was added to a solution of the amino altroside in water, methyl alcohol, or acetone. The experiments were carried out at 55, 60, 70, and 100° over 7-18 hours. The solvent was removed under vacuum, and the dry residue was washed with a small amount of water, dried and investigated (melting point, properties of the hydrochloride and picrate). In all experiments the 2-desoxy-2-amino-4, 6-benzylidene- α-methyl altroside was obtained back unchanged. The formation of a mercaptan by the decomposition of S-methylisothiourea was noted.

An attempt to obtain the guanido derivative by the action of O-methylisourea on 2-desoxy-2-amino-4, 6-benzylidene-α-methyl altroside resulted in an insignificant yield of the required compound. To 5 g of the amino compound in a flask with a ground glass stopper a solution of O-methylisourea, obtained from its hydrochloride (7 g) in methyl alcohol by means of sodium alcoholate, was added. The solution was kept 2 weeks at room temperature. The yield was 3 g of a substance (after washing with water) which formed a hydrochloride with m. p. 129-130° and a picrate with m. p. 160-161°, which did not give melting point depressions when mixed with the corresponding amino altroside derivatives. The aqueous solution (from the washing) gave a strong color test for the guanido group. The presumed guanido compound formed a picrate with m. p. 118-122°, which could not be further purified and compared with the picrate of the guanido compound described below, with m. p. 127-128°.

4. 2-Desoxy-2-methylamino-4, 6-benzylidene-α-methyl altroside (V)

Methylamine was obtained in the usual way by warming 38% aqueous formaldehyde solution with ammonium chloride. Fractional crystallization was used to isolate the salt, which was purified by recrystallization from anhydrous methyl alcohol and then from n-butyl alcohol, as ammonium chloride is completely insoluble in the latter. A solution of the pure methylamine hydrochloride in anhydrous methyl alcohol was added to a hot sodium methylate solution, and the gaseous methylamine was absorbed in anhydrous methyl alcohol at room temperature. An autoclave containing 10 g of the anhydro sugar and 220 ml of anhydrous methyl alcohol with 5.2 g of methylamine, was heated 35 hours at 100°. The anhydride reacted completely. The slightly yellowish solution extracted from the autoclave was evaporated under vacuum to remove methyl alcohol and methylamine, and the residue was dissolved in acetone. On cooling to −10° a dense mass of small crystals was formed, which were recrystallized from a small amount of hot acetone. Slow cooling resulted in the formation of large transparent crystals with m. p. 124-125°. The yield was 9.3 g (83%).

The substance did not contain any crystallization solvent.

By its analytical data (m. p. 125-126°) the substance corresponds to the methylamine derivative of a benzylidene methyl hexoside.

Found %: N 4.91 (average of two analyses). $C_{15}H_{21}O_5N$. Calculated %: N 4.73.

By analogy with the amino derivative it may be given the structure of 2-desoxy-2methylamino-4, 6-benzylidene-α-methyl altroside.

The methylamine derivative is soluble in alcohol, acetone and chloroform, and with difficulty in hot water. The aqueous alcoholic solution of the base does not color phenolphthalein; it forms salts with strong acids.

The hydrochloride was prepared by the dropwise addition of a 3% solution of hydrogen chloride in dry acetone to an acetone solution of the base cooled to +5°, till neutral to methyl orange. The crystalline substance formed was recrystallized from aqueous acetone. The salt forms transparent rectangular plates, is easily soluble in aqueous and with difficulty in anhydrous acetone. After drying the salt had m. p. 135-136°

The methylamine derivative readily forms a picrate if an aqueous solution of picric acid saturated in the cold is added to a dilute solution of the base. Recrystallization from hot aqueous 20% methyl alcohol yielded golden-yellow fine needles easily soluble in alcohol. After being dried in a vacuum over phosphoric anhydride, the picrate of 2-desoxy-2-methylamino-4, 6-benzylidene-α-methyl altroside had m. p. 165-166°.

5. The Action of Guanidine and its Derivatives on 2, 3-Anhydro-4, 6-Benzylidene -α-Methyl Altroside

The experiments were performed with guanidine and monoacetylguanidine in methyl alcohol, with guanidine in aqueous acetone and pyridine solutions, and with guanidine hydrochloride in methyl alcohol.

The guanido derivative could be synthesized only by the action of guanidine in pyridine solution [14]. This base favored the addition of methyl alcohol at the α-oxide ring, while guanidine hydrochloride converted the anhydro derivative into 3-chloro-4, 6-benzylidene-α-methyl glucoside.

a) A guanido sugar derivative, typified by 2-desoxy-2-guanido-4, 6-benzylidene-α-methyl altroside (VI) was synthesized from 2, 3-anhydro-4, 6-benzylidene-α-methyl alloside (III) by heating it with guanidine in aqueous pyridine solution [14] 10 hours on the water bath, at 100°. 15 g of guanidine hydrochloride was used to obtain, by the action of alcoholate, and after removal of sodium chloride and evaporation of the alcohol, a thick syrup of the free guanidine, which was then dissolved in 40 ml of pyridine with the addition of 2 ml of water to make the dissolution complete. Fission of the oxide ring was complete. After evaporation of the pyridine under vacuum with additions of water till the odor of pyridine ceased, a residue was obtained in the form of a viscous mass, easily soluble in acetone, but which did not crystallize from this solvent when cooled to 0°. The viscous mass was repeatedly extracted with warm ethyl ether, which extracted a very small amount of the product, and with chloroform. The chloroform extract yielded a dark yellow syrup which partly crystallized on standing. 4.6 g of a hygroscopic substance was obtained and recrystallized from acetone, m. p. 145-147° (after drying over phosphorus pentoxide at 20°). The substance dissolves in water to give a strongly alkaline solution, and gives the guanido group reaction (intense crimson color).

Found %: N 13.35 (average of 2 analyses). $C_{15}H_{21}O_5N_3$. Calculated %: N 13.00.

The picrate after recrystallization from aqueous alcohol had m. p. 127-128°.

An acetone solution of the strongly alkaline base was neutralized by carbon dioxide, and ether was added to obtain a crystalline precipitate which had m. p. 151-152° after drying; the substance was the carbonate of 2-desoxy-2-guanido-4, 6-benzylidene- α-methyl altroside (VI), by analogy with the amino derivative obtained from the 2, 3-anhydro alloside by the action of ammonia. Thus, the reaction of guanidine in pyridine (and possibly in another non-reacting solvent) with 2, 3-anhydro sugars is a convenient guanidation method.

Guanidine in acetone solution did not form a guanido derivative. Guanidine was prepared from guanidine carbonate through guanidine sulfate, the removal of the sulfate group being effected by means of barium hydroxide. The clear guanidine solution was evaporated in a vacuum to remove the solvent, dissolved in acetone with the addition of a small amount of water, and the solution was heated 30 hours in an autoclave at 100°. 5.3 g of the 10 g of anhydride used was obtained back unchanged, while the remaining product could not be purified because of strong resinification.

b) The action of an alcoholic guanidine solution on 2, 3-anhydro-4, 6-benzylidene-α-methyl alloside led to alcohol addition; it was proved that the product had the structure of 2-methyl-4, 6-benzylidene-α-methyl altroside (VII), on the basis of literature data.

A solution of the anhydro sugar (15 g) and guanidine (12-25 g) in anhydrous methyl alcohol was heated 32-39 hours in an autoclave at 100°. After removal of the alcohol the residue was extracted several times with ether; the ether extract yielded a glassy mass which was converted gradually into a crystalline substance in the form of large transparent crystals when a previously warmed solution in acetone was very slowly cooled. In order to complete the separation, a well-formed crystal was introduced into the mother liquor evaporated to a small volume; the crystal continued to grow up to a certain limit. The large crystals obtained were recrystallized from acetone. The crystals contained no solvent, as was proved by the absence of any loss in weight during drying, and the constant m. p. 97-98°.

The substance is easily soluble in anhydrous and aqueous alcohol as well as in acetone, has a neutral reaction, and contains no nitrogen. The properties of this substance agree with the properties of 2-methyl-4, 6-benzylidene-α-methyl altroside as given in the literature [13].

In order to show the products to be identical this methylated derivative was prepared by the usual method – by the action of heat (12 hours) on the water bath with excess of sodium methylate in anhydrous methyl alcohol. The substance was obtained from methyl alcohol solution in the form of prismatic crystals with m. p. 98-99°. A sample of the substance obtained in the attempt to effect guanidation in methyl alcohol, mixed with the substance known from literature data to be 2-methyl-4, 6-benzylidene-α-methyl altroside, gave no melting point depression.

The above methylated derivative was also obtained when the 2, 3-anhydro monose was heated with monoacetylguanidine, which was prepared from guanidine by heating it with ethyl acetate 15 minutes on the water bath. The crystals of monoacetylguanidine which formed on cooling (yield 90%) had m. p. 143-144° (instead of the 145° given in the reference books). 10 g of the anhydro sugar, 10 g of monoacetylguanidine, and 200 ml of anhydrous methyl alcohol were heated together 49 hours in an autoclave at 130°. 1.6 g of the anhydro sugar was obtained back unchanged. The remaining syrup was extracted with ether to give a glassy substance, which, after recrystallization from acetone, was obtained in the form of large transparent crystals (8.3 g), and which proved to be 2-methyl-4, 6-benzylidene-α-methyl altroside (m. p. 97-98°).

c) The action of guanidine hydrochloride on 2, 3-anhydro-4, 6-benzylidene-α-methyl alloside gave a chloro substituted derivative, as the result of hydrogen chloride addition at the α-oxide ring; the reaction products yielded the 3-desoxy-3-chloro-4, 6-benzylidene-α-methyl glucoside (VIII) which had already been prepared by other authors [13], but by a more complicated route.

A mixture of the 2, 3-anhydro sugar (10 g), dry guanidine hydrochloride (10 g) and 200 ml of anhydrous methyl alcohol was heated 60 hours in an autoclave at 140°. 4.8 g of unreacted anhydro sugar was obtained, which showed that the α-oxide ring reacts slowly in such conditions. The residue (3.7 g), after removal of the precipitate consisting of the unreacted anhydride and of the solvent, was dissolved in a small amount of hot methyl alcohol. The fine crystals of the original anhydride which were additionally deposited when the solution was cooled were filtered off, the solution was evaporated under vacuum, and the halogenated substance was recrystallized from aqueous acetone; the product was obtained pure in the form of light, small, shiny leaflets, insoluble in hot water, easily soluble in alcohol, acetone, chloroform, and benzene. After vacuum drying over phosphorus pentoxide the substance had m. p. 162°. The Beilstein test for halogens was strongly positive, but chlorine was not detected by silver nitrate in aqueous alcoholic solution. When the alcoholic solution was heated with a drop of 0.5 N sulfuric acid solution, an odor of benzaldehyde was noted, as was to be expected. Guanidine hydrochloride and guanidine were extracted from the wash waters, but no guanido derivative of the monose was detected.

SUMMARY

1. 2, 3-anhydro-4, 6-benzylidene-α-methyl alloside was obtained from 4, 6-benzylidene-α-methyl glucoside by way of the tosyl derivative. The method for the preparation and purification of the ditosyl derivative has been improved, and the best conditions for its reaction with sodium methylate, with regard to temperature and ratio of the reagents, have been found.

2. It was found that the interaction of 1, 2–5, 6-diisopropylidene-3-tosylglucofuranose and 1, 2–3, 4-diisopropylidene-6-tosylgalactose with alcoholic guanidine solution on heating results only in hydrolysis of the tosyl (toluene sulfonic acid) group, and not in guanidation.

3. Cellulose methyl sulfonate and sulfate esters exchange their ester groups for ammonia residues only to a small extent by the action of liquid ammonia or when heated in an autoclave with gaseous ammonia in contrast to the easily aminated oxycelluloses (oxidized by periodic acid).

4. 2-desoxy-2-amino-4, 6-benzylidene-α-methyl altroside, 2-desoxy-2-methylamino-4, 6-benzylidene-α-methyl altroside and their hydrochlorides and picrates were obtained in pure form from 2, 3-anhydro-4, 6-benzylidene-α-methyl alloside.

The location of the amino group at the second carbon atom in the monose was confirmed by the preparation of 2-acetamido-3-acetyl-4, 6-benzylidene-α-methyl altroside.

5. The reaction of 2, 3-anhydro-4, 6-benzylidene-α-methyl alloside with free guanidine in pyridine (but not in alcohol) solution results in the formation of a guanido derivative as the result of guanidine addition at the α-oxide ring. Experiments on the preparation of a guanido derivative from 2-desoxy-2-amino-4, 6-benzylidene-α-methyl altroside by the action of O-methylisourea and particularly of S-methylisothiourea met with little success, in contrast to the previously described positive results with 5, 6-anhydroglucose.

6. Free guanidine and also monoacetyl guanidine in alcoholic solution break the 2, 3-anhydro ring with addition of the alcohol, analogously to the action of alcoholates, to form 2-methyl-4, 6-benzylidene-α-methyl altroside.

7. The reaction of 2, 3-anhydro-4, 6-benzylidene-α-methyl altroside with guanidine hydrochloride gives 3-desoxy-3-chloro-4, 6-benzylidene-α-methyl glucoside.

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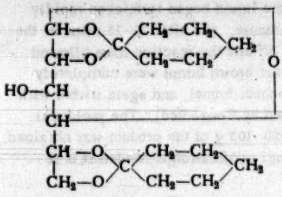
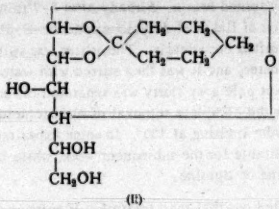
CONDENSATION OF GLUCOSE WITH HYDROAROMATIC KETONES

M. Kh. Gluzman and N. P. Klyushnik

The condensation reaction of glucose with aliphatic ketones has long been known, and the action of acetone [1, 2] has been studied in greatest detail. It is also known that glucose does not condense with atomatic and aliphatic-aromatic ketones. As regards the hydroaromatic ketones, Hockett and his co-workers [3] showed that cyclohexanone reacts with glucose to form 1, 2:5, 6-bicyclohexylidene-D-glucofuranose (I), which by hydrolysis by means of a methanol solution of hydrogen chloride gave 1, 2-cyclohexylidene-D-glucofuranose (II).



(I)



(II)

These authors report that they specially carried out 14 experiments with the object of raising the yields of bicyclohexylidene-D-glucofuranose, by varying the proportions of glucose and cyclohexanone, the duration of heating, and the amount of sulfuric acid, but did not obtain yields above 43%. V. F. Kazimirova [4] reacted cyclohexanone with monoses and polyhydric alcohols in benzene, ethyl ether, and ligroine. In the case of 5 compounds the yields of the condensation products were about 45%, and only tricyclohexylidene mannitol was obtained in 58.7% yield. The time used for the condensation of cyclohexanone with monoses and polyhydric alcohols, both by Kazimirova and by Hockett and co-workers, was 12 hours, followed by prolonged crystallization overnight or during twenty-four hours.

We studied the condensation reaction between glucose and cyclopentanone and cyclohexanone. With the first ketone there is practically no reaction. For the condensation of glucose with cyclohexanone we succeeded in developing two methods for the preparation of cyclohexanone derivatives, which have a number of advantages over those described above. One method gives a yield of bicyclohexylidene-D-glucofuranose (I) of the order of 53%, and the other, 75-85%, which is double the yield obtained by Hockett. In addition, the time required for the experiment is much shorter – 1 hour instead of 12, and no supplementary crystallizations are required for the preparation of pure bicyclohexylidene-D-glucofuranose. Hydrolysis of the latter to 1, 2-cyclohexylidene-D-glucofuranose (II) may be effected by Hockett's method, which gives a

74% yield. If the bicyclohexylidene-D-glucofuranose is hydrolyzed by means of dilute acetic acid, in the same way as diacetoneglucose [5], the yield of cyclohexylidene-D-glucofuranose (II) is 40%.

EXPERIMENTAL *

Preparation of 1, 2 : 5, 6-bicyclohexylidene-D-glucofuranose (I). Method 1. Glucose and cyclohexanone (1:6) were placed in a wide-necked jar fitted with a mechanical stirrer, and then 15-20 ml of sulfuric acid (d = 1.84) for each 50 g of glucose was added in a thin stream with vigorous stirring. There was a considerable rise of temperature (up to 40-45°) and the reaction mass gradually turned brown. After 30-40 minutes the glucose dissolved completely. Anhydrous soda was then added to the transparent brown liquid and the stirring was continued; the solution rapidly became lighter in color and at the end of the neutralization became yellow. The neutralization (to Congo Red) was completed in 10-15 minutes (when acetone is used, the neutralization lasts 10-20 hours). Sodium sulfate and excess soda were filtered off and the filtrate was distilled under vacuum (to drive off excess cyclohexanone and its condensation products), the temperature of the water bath being gradually raised to 80-90°. The reaction product was then extracted from the syrup by means of ligroine or gasoline. The gasoline solution (preferably cooled in ice) deposited white crystals of bicyclohexylideneglucofuranose with m. p. 130-131°. After a second crystallization the m. p. was 134-135°. The weight of the product was usually equal to the weight of the original glucose.

Method 2. 65 g of anhydrous glucose passed through a fine sieve was placed in a wide-necked jar fitted with a stirrer, 80-85 ml of cyclohexanone and 50 ml of dioxane was added, and then 15-20 ml of sulfuric acid (d = 1.84) was introduced in a thin stream with vigorous stirring. The reaction mass became hot and rapidly turned brown. Already after 5-7 minutes the liquid began to thicken rapidly because of the formation of flakes of dicyclohexylidene-D-glucofuranose, and after 10-15 minutes the contents of the jar solidified completely. The stirrer was switched off and the reaction mass allowed to stand another 30 minutes, and it was then stirred with water till the brown lumps were completely broken up. The resultant pale grey slurry was separated off on a Buchner funnel, and again stirred with water once or twice for the complete removal of sulfuric acid (tested by Congo Red). The yield was 80-95 g of a white powder melting at 130°. In some experiments 100-103 g of the product was obtained. This product is quite suitable for the subsequent work, while if a final purification is needed it is re-crystallized fromgasoline or ligroine.

It must be pointed out that such treatment is quite impossible in the acetonation of glucose, as in that reaction the presence of water is quite inadmissible not only during the condensation but immediately after (the product is hydrolyzed).

Preparation of 1, 2-cyclohexylidene-D-glucofuranose (II). Method 1. 150 ml of 75% acetic acid was added to 50 g of bicyclohexylidene-D-glucofuranose (m. p. 128-130°) and the latter dissolved on the water bath (65-70°) with frequent shaking. The solution usually turned various shades of crimson. When the solution process was complete, the hydrolysis was continued at the same temperature during 30-45 minutes, and the acetic acid was then driven off under vacuum. The dry white or slightly colored residue in the flask was treated with a small amount of ether and recrystallized from a mixture of alcohol and ethyl acetate (1:3). Pure white needle-shaped crystals melting at 151° were obtained. After repeated crystallization from a mixture of alcohol and ethyl acetate the m. p. was 151-152°. Yield 15-20 g.

Method 2. The hydrolysis was carried out as in Method 1, but the acetic acid was not distilled off, but neutralized by ammonia after the addition of 50-100 ml of water; the solution turned yellow, and an oil separated out on the bottom of the flask and solidified on colling. The oily layer was not separated, and 30-50 ml of amyl acetate (or ethyl acetate) was added to the warm solution which was

* A. A. Tapeshkina participated in the experimental work.

left to crystallize. On the following day the crystals were separated off, washed lightly with alcohol, and dried. The yield was 13-15 g from 50 g of the bicyclohexylidene derivative, m. p. 149-150°.

SUMMARY

The method for the preparation of 1, 2 : 5, 6-bicyclohexylidene-D-glucofuranose has been improved to make possible the preparation of the pure substance in a short time with 75-85% yields.

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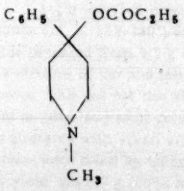
SYNTHETIC ANALGESICS

III. ESTERS OF 1-PHENYL-1-ALKYL-2-METHYL-3-DIALKYLAMINOPROPAN -1-OLS

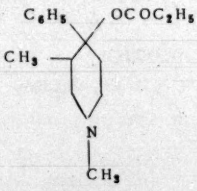
I. I. Nazarov and E. M. Cherkasova

In the previous communications [1, 2] we described a number of new esters of 1-phenyl-1-alkyl-3-dialkylaminopropan -1-ols, which included some powerful anesthetics of low toxicity. In an extension of our investigation program it appeared of interest to synthesize similar esters with methyl radicals in the propanol chain.

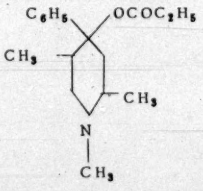
The literature contains many instances which illustrate the favorable effect of such substitution on the activity of anesthetics and analgesics. For example, the introduction of one or two methyl groups into the piperidine nucleus intensifies considerably the analgesic activity of 4-phenyl-4-piperidol propionate [3, 4]:



Nornisentyl
(0.3)



Nisentyl
(1-5)



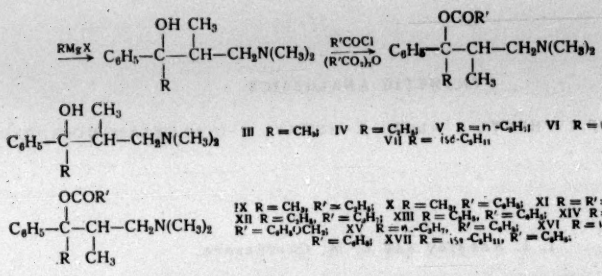
Promedol
(2-5)

(the analgesic activity in comparison with morphine is given in parentheses).

The introduction of a methyl group has a similar effect on analgesic activity also in other compounds, for example, in the phenadone series [5]; it was therefore decided to synthesize 1-phenyl-1-alkyl-2-methyl-3-dialkylaminopropan -1-ol esters in order to determine the influence of the methyl group in the propanol chain on the physiological (anesthesizing) activity of these compounds.

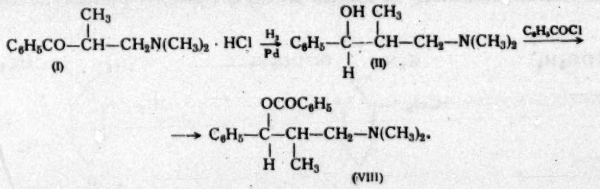
The synthesis was carried out according to the following scheme:

$$C_6H_5COCH_2CH_3 \xrightarrow[CH_2O]{NH(CH_3)_2 \cdot HCl} C_6H_5COCHCH_2N(CH_3)_2 \cdot HCl \longrightarrow$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\quad CH_3 \qquad\qquad\qquad\qquad\qquad\qquad\quad (I)$$



Phenyl-β-dimethylaminoisopropyl ketone hydrochloride was obtained in 80 % yield by means of the Mannich reaction from propiophenone, dimethylamine hydrochloride, and paraformaldehyde, and by means of Grignard reagents (3-fold excess) it was converted in 60-86% yields into tertiary amino alcohols, which were esterified with the aid of acid chlorides (sometimes anhydrides) to give the corresponding esters (30-78% yields).

Catalytic hydrogenation of phenyl β-dimethylaminoisopropyl ketone over Pd catalyst also gave the corresponding secondary amino alcohol, which was esterified by benzolyl chloride to give the corresponding benzoate:



All the esters synthesized form hydrochlorides and other salts which are easily soluble in water.

In most instances the ester hydrochlorides were isolated direct in the esterification of amino acids by acid chlorides.

In the synthesis of the propionate (XI), the hydrochlorides of two diastereoisomers were isolated. The action of propionic anhydride on the amino alcohol (IV) gave the hydrochloride the α-isomer (m. p. 169-170°), while the action of propionyl chloride gave the hydrochloride the β-isomer (m. p. 145-146°).

Most of the amino acids described in this paper are low-melting crystalline compounds with an amine odor, which are easily soluble in organic solvents. The hydrochlorides of these amino alcohols, and of their esters, are colorless substances which crystallize well and are soluble in water.

Some of the compounds synthesized were subjected to pharmacological investigation and showed interesting physiological activity.* The most interesting substance proved to be 1-ethyl-1-phenyl-2-methyl-

* The tests were performed by M. D. Mashkovsky at the S. Ordzhonikidze All-Union Scientific Research Institute for Pharmaceutical Chemistry.

3-dimethylaminopropan -1-ol (XIV) phenoxyacetate, which is a very powerful anesthetic, not inferior to dicaine in strength.

EXPERIMENTAL

The propiophenone used as the starting material (b. p. 213-214°) was obtained in 85% yield from propionyl chloride and benzene in the presence of aluminum chloride by means of the Friedel-Crafts reaction.

Phenyl β-dimethylaminoisopropyl ketone (I) [6]. To a solution of 47.5 g of propiophenone in 80 ml of alcohol 38 g of dimethylamine hydrochloride, 15.8 g of paraformaldehyde, and 2-3 ml of hydrochloric acid was added. After removal of the alcohol under a slight vacuum the residue was treated with dry ether. The yield was 60 g of phenyl β-dimethylaminoisopropyl ketone hydrochloride (I) with m. p. 142-143° (from acetone).

2-Methyl-1-phenyl-3-dimethylaminopropan -1-ol (II). 9 g of the amino ketone (I) hydrochloride (m. p. 143-144°) in 100 ml of anhydrous methanol was hydrogenated in the presence of 4.42 g of Pd catalyst on calcium carbonate. The amount of hydrogen absorbed was 1060 ml instead of the theoretically required 997 ml. The catalyst was filtered off, the alcohol removed, and the residue treated with alkali. The base obtained was extracted with ether and dried by sodium sulfate. After removal of the ether, 4.5 g of large crystals of 2-methyl-1-phenyl-3-dimethylaminopropan -1-ol (II) with m. p. 88-89° was obtained.

Found %: C 74.44, 74.31; H 10.65, 9.22; N 7.05, 6.78. $C_{12}H_{19}ON$. Calculated %: C 74.5; H 9.8; N 7.2.

The hydrochloride of the amino alcohol (II) melted at 170-171° (from acetone).

Found %: N 5.86, 5.76. $C_{12}H_{20}ONCl$. Calculated %: N 6.1

1,2-Dimethyl-1-phenyl-3-dimethylaminopropan -1-ol (III). 12 g of the amino ketone (I) hydrochloride (m. p. 139-140°) was gradually added with vigorous stirring to a solution of methylmagnesium iodide prepared from 4.1 g of magnesium and 24.5 g of methyl iodide in 60 ml of anhydrous ether, cooled by a mixture of ice and salt. The hydrochloride was added at such a speed that the temperature of the reaction mass did not rise above 0°. The following day the mixture was stirred 4 hours at the boiling point of ether and after cooling was hydrolyzed by means of 18% hydrochloric acid. The aqueous layer was saturated with alkali and the base which separated was repeatedly extracted with ether. The ether extracts were dried by sodium sulfate, the ether was distilled off, and the product distilled under vacuum. The yield was 8.7 g (80%) of 1, 2-dimethyl-1-phenyl-3-dimethylaminopropan -1-ol (III), with b. p. 90-91° at 1.5 mm. After 3 weeks the whole mass crystallized , and melted at 42-43°.

Found %: C 75.25, 75.72; H 10.38, 9.74; N 6.93, 7.07. $C_{13}H_{21}ON$. Calculated %: C 75.4; H 10.03; N 6.75.

The hydrochloride melted at 179-180° (from a mixture of acetone and chloroform).

Found %: C 63.82, 63.86; H 8.94, 8.88; N 5.90, 5.62. $C_{13}H_{22}ONCl$. Calculated %: C 64.4; H 9.1; N 5.7.

1-Ethyl-1-phenyl-2-methyl-3-dimethylaminopropan -1-ol (IV). 34.1 g of the amino ketone (I) hydrochloride was added with cooling and vigorous stirring to a solution of ethylmagnesium bromide prepared from 11.8 g of magnesium and 36 ml of ethyl bromide in 140 ml of anhydrous ether. The following day the reaction mixture was heated 4 hours at the boiling point of ether and then treated as in the previous experiment. The yield was 28.5 g (86%) of 1-ethyl-1-phenyl-2-methyl-3-dimethylaminopropan -1-ol (IV), with b. p. 126-128° at 5 mm. At the end of 3 weeks the amino alcohol (IV) crystallized and melted at 32-33°.

Found %: C 75.93, 76.13; H 10.25, 9.31; N 6.72, 6.38. $C_{14}H_{23}ON$. Calculated %: C 75.7; H 10.4; N 6.33.

The hydrochloride of the amino alcohol (IV) melted at 177.5-178.5° (from acetone-alcohol mixture).

Found %: C 64.76, 64.69; H 9.61, 9.27; N 5.50, 5.16. $C_{14}H_{24}ONCl$. Calculated %: C 65.2; H 9.4; N 5.4.

1-n-Propyl-1-phenyl-2-methyl-3-dimethylaminopropan-1-ol (V). 22.7 g of the amino ketone (I) hydrochloride (m. p. 141-142°) was slowly added to a solution of n-propylmagnesium bromide prepared from 7.2 g of magnesium and 37 g of n-propyl bromide in 85 ml of anhydrous ether at −2-0°. The following day the reaction mass was heated 5 hours with stirring on the water bath. The subsequent treatment was as described for the preceding experiment.

The yield was 14.2 g (60%) of 1-n-propyl-1-phenyl-2-methyl-3-dimethylaminopropan-1-ol (V) with b. p. 109-111° at 1 mm, a slowly crystallizing oil.

Found %: C 76.33, 76.31; H 10.65, 10.37; N 5.83, 5.89. $C_{15}H_{25}ON$. Calculated %: C 76.5; H 10.7; N 5.93.

The hydrochloride of the amino alcohol (V) melted at 174-175° (from acetone-ether mixture).

Found %: C 66.17, 66.68; H 9.87, 9.78; N 5.22, 5.14. $C_{15}H_{26}ONCl$. Calculated %: C 66.0; H 9.7; N 5.16.

1-n-Butyl-1-phenyl-2-methyl-3-dimethylaminopropan-1-ol (VI). 9.5 g of the amino ketone (I) hydrochloride was added with thorough cooling to a solution of n-butylmagnesium bromide prepared from 3 g of magnesium and 14.7 g of n-butyl bromide in anhydrous ether. The next day, after heating 3 hours and the usual treatment as described for the preceding experiment, 6.07 g (59%) of 1-n-butyl-1-phenyl-2-methyl-3-dimethylaminopropan-1-ol (VI) with b. p. 117-120° at 1 mm was obtained.

Found %: C 76.71, 77.05; H 10.85, 10.66; N 5.89, 5.63. $C_{16}H_{27}ON$. Calculated %: C 77.1; H 10.88; N 5.6.

The hydrochloride of the amino alcohol (VI) melted at 158-159° (from acetone).

Found %: N 4.66, 4.52. $C_{16}H_{28}ONCl$. Calculated %: N 4.48.

1-Isoamyl-1-phenyl-2-methyl-3-dimethylaminopropan-1-ol (VII). 22.7 g of the amino ketone (I) (m. p. 141-142°) was gradually added with thorough cooling to a solution of isoamylmagnesium-bromide prepared from 5.75 g of magnesium and 37.8 g of isoamyl bromide (b. p. 117-118°) in anhydrous ether. The next day, after heating 4 hours and the usual treatment as described for the preceding experiment, 3.45 g of 1-isoamyl-1-phenyl-2-methyl-3-dimethylaminopropan-1-ol was obtained.

B. p. 120-122° at 1.5-2 mm, n_D^{20} 1.5033, d_4^{20} 0.9451. MR_D 82.2; Calc. 82.5.

Found %: N 5.83, 5.73. $C_{17}H_{29}ON$. Calculated %: N 5.32.

In addition, the hydrochloric acid layer yielded 17 g of the sparingly soluble hydrochloride of the alcohol (VII), with m. p. 147-148°. The total yield was 70%.

Found %: N 4.36, 4.18. $C_{17}H_{30}ONCl$. Calculated %: N 4.66.

1-Phenyl-2-methyl-3-dimethylaminopropan-1-ol benzoate (VIII). 2.75 ml of freshly distilled bensoyl chloride in 3 ml of dry benzene was added to a solution of 1.95 g of the amino alcohol (II) in 8 ml of dry benzene. After several minutes the whole mass crystallized. The mixture was heated at 80-90° 1 hour and then left overnight. The following day 10 ml of anhydrous ether was added, the mixture was warmed for a few minutes, and the precipitate was filtered off. 3.5 g of crystals with m. p. 156° was obtained which were then purified by warming with acetone and recrystallization from acetone-alcohol mixture. The result was 2.2 g (78%) of the hydrochloride of 1-phenyl-2-methyl-3-dimethylaminopropan-1-ol benzoate (VIII) with m. p. 186-188°.

Found %: C 68.36, 68.36; H 7.24, 6.95; N 4.09, 4.26. $C_{19}H_{24}O_2NCl$. Calculated %: C 68.36; H 7.2; N 4.19.

1, 2-Dimethyl-1-phenyl-3-dimethylaminopropan -1-ol propionate (IX). a) To a solution of 1 g of the amino alcohol (III) in 5 ml of anhydrous ether, 1.5 g of freshly distilled propionyl chloride (b. p. 78-79°) * was added. The whole mass crystallized almost at once. After 1.5 hours the precipitate was filtered off, washed several times in ether, and recrystallized from 5 ml of dry acetone. The yield was 0.5 g of the hydrochloride of 1, 2-dimethyl-1-phenyl-3-dimethylaminopropan -1-ol propionate (IX) with m. p. 145°.

Found %: C 63.59, 63.79; H 8.65, 8.44; N 4.93, 4.69. $C_{16}H_{26}O_2NCl$. Calculated %: C 64.1; H 8.4; N 4.7.

b) To a solution of 1.7 g of the amino alcohol (III) in 4 ml of dry benzene, 2.2 ml of propionic anhydride in 2 ml of benzene and several crystals of trichloroacetic acid were added. On the following day the partly crystallized mass was heated for 2 hours at 80°. The solvents were driven off under a slight vacuum, the residue acidified with 20% hydrochloric acid, the neutral products extracted with ether, and the aqueous layer treated with soda. The base which separated out was extracted with ether and distilled under vacuum after being dried with sodium sulfate. The yield was 1.25 g of 1, 2-dimethyl-1-phenyl-3-dimethylaminopropan -1-ol propionate (IX), with b. p. 108-110° at 1 mm.

Found %: C 72.14, 72.72; H 9.59, 9.19; N 5.28, 5.62. $C_{16}H_{25}ON$. Calculated %: C 72.5; H 9.5; N 5.32.

The action of dry hydrogen chloride on an ether solution of this propionate gave 1.1 g of the hydrochloride with m. p. 169-171° (from an acetone-ether mixture).

Found %: C 64.08, 63.74; H 8.30, 8.67; N 4.82, 4.5. $C_{16}H_{26}O_2NCl$. Calculated %: C 64.1; H 8.4; N 4.7.

1,2-Dimethyl-1-phenyl-3-dimethylaminopropan -1-ol benzoate (X). 2.06 g of the amino alcohol (III) (m. p. 42°), 0.3 g of magnesium, 15 ml of dry benzene, and 2.8 ml of benzoyl chloride was taken. A precipitate was formed. On the following day the mixture was heated 6 hours on the water bath and 2 hours with an added portion of ether. The residue was filtered off and recrystallized from acetone with the addition of a few drops of anhydrous alcohol. The yield was 2.5 g (73%), m. p. 180°; after two further recrystallizations the hydrochloride of 1, 2-dimethyl-1-phenyl-3-dimethylaminopropan -1-ol benzoate (X) with m. p. 181-183° was obtained. Yield 1 g.

Found %: N 4.29, 4.07. $C_{20}H_{26}O_2NCl$. Calculated %: N 4.03.

1-Ethyl-1-phenyl-2-methyl-3-dimethylaminopropan -1-ol propionate (XI). 2.2 g of the amino alcohol (IV) in 8 ml of benzene, 2.8 ml of propionic anhydride, and about 1 g of trichloroacetic acid was taken. The whole mass crystallized after 0.5 hour. On the following day the mixture was heated 5 hours on the water bath, when the precipitate dissolved.

The mixture was then treated in the usual way, as described for the preparation of the propionate (IX), Method b. The 1-ethyl-1-phenyl-2-methyl-3-dimethylaminopropan -1-ol propionate base (XI) with b. p. 113-115° at 1.5 mm was obtained in a yield of 1.8 g (64%).

Found %: C 73.47, 73.30; H 9.86, 10.10; N 5.01, 4.87. $C_{17}H_{27}O_2N$. Calculated %: C 73.6; H 10.0; N 5.05.

The hydrochloride of the propionate (XI) melted at 200-202° (from acetone-chloroform mixture).

* The propionyl chloride was distilled in the presence of 10 % by weight of dimethylaniline.

Found %: N 4.49. $C_{17}H_{28}O_2NCl$. Calculated %: N 4.46.

1-Ethyl-1-phenyl-2-methyl-3-dimethylaminopropan -1-ol butyrate (XII). 2.2 g of the amino alcohol (IV), 2 ml of freshly distilled butyryl chloride (b. p. 93-95°) and 5 ml of toluene was taken. Heat was evolved and a precipitate formed. After standing 2 days, the mixture was heated 2 hours on the boiling water bath. Anhydrous ether was then added, and the mixture again heated about 1 hour. The ether was poured off the residue, and another portion of ether was added, which was also decanted. The subsequent treatment was as in the preceding experiment. The yield was 1.05 g of 1-ethyl-1-phenyl-2-methyl-3-dimethylaminopropan -1-ol butyrate (XII) with b. p. 120-122° at 1.5-2 mm (and also a small amount of a lower boiling fraction, 1 g).

Found %: C 74.43, 74.02; H 10.43, 9.92; N 4.40, 4.55. $C_{18}H_{29}O_2N$. Calculated %: C 74.2; H 10.0; N 4.8.

The hydrochloride of the butyrate (XII) has m. p. 191-192° (from a mixture of acetone, alcohol and ether).

Found %: C 65.81, 66.36; H 9.13, 9.00; N 4.60 4.44. $C_{18}H_{30}O_2NCl$. Calculated %: C 66.01; H 9.2; N 4.28.

1-Ethyl-1-phenyl-2-methyl-3-dimethylaminopropan -1-ol benzoate (XIII). 2.2 g of the amino alcohol (IV), 2.8 g of benzoyl chloride, 0.3 g of magnesium, and 8 ml of dry benzene were taken. The next day the whole mass crystallized. The subsequent treatment was as described for the preceding experiment. 1.1 g of the benzoate base (XIII) with b. p. 160-170° at 1 mm was obtained and at once converted into the hydrochloride. The yield was 1.1 g of the hydrochloride of 1-ethyl-1-phenyl-2-methyl-3-dimethylaminopropan -1-ol benzoate with m. p. 176-178° (from acetone).

Found %: C 69.22, 69.25; H 7.34, 7.71; N 3.90, 4.15; $C_{21}H_{28}O_2NCl$. Calculated %: C 69.6; H 7.5; N 3.87.

1-Ethyl-1-phenyl-2-methyl-3-dimethylaminopropan -1-ol phenoxyacetate (XIV). 2.2 g of the amino alcohol (IV) in 16 ml of anhydrous ether was taken, and about 0.1 g of magnesium and 2.2 g of phenoxyacetyl chloride (b. p. 111-113° at 13 mm) added. The following day the partly crystallized substance was washed several times with ether and then dissolved in a mixture of dry acetone and anhydrous alcohol. The precipitate formed (0.3 g) was the original alcohol (IV) and gave no melting point depression with a known sample. The mother liquor, after partial removal of the solvents, yielded 1 g of the hydrochloride of 1-ethyl-1-phenyl-2-methyl-3-dimethylaminopropan -1-ol phenoxyacetate (XIV), with m. p. 147-148° (from a mixture of acetone and ethyl acetate).

Found %: N 3.57, 3.47. $C_{22}H_{30}O_3NCl$. Calculated %: N 3.6.

1-n-Propyl-1-phenyl-2-methyl-3-dimethylaminopropan -1-ol benzoate (XV). 2.35 g of the amino alcohol (V), 0.3 g of magnesium, 3.28 g of benzoyl chloride, and 16 ml of dry benzene was taken. After several days the mixture was heated 3 hours at the boiling point of benzene. The subsequent treatment was as described for the preparation of the benzoate (XIII). After vacuum distillation a thick oil (0.7 g) was obtained, which was converted into the hydrochloride with m. p. 182-184° (from acetone and ether).

Found %: N 3.67, 3.73. $C_{22}H_{30}O_2NCl$. Calculated %: N 3.72.

1-n-Butyl-1-phenyl-2-methyl-3-dimethylaminopropan -1-ol benzoate (XVI). 2.5 g of the amino alcohol (VI), 2.25 g of benzoyl chloride, 0.3 g of magnesium, and 10 ml of dry benzene was taken. A precipitate gradually formed. The following day the reaction mass was treated in the usual way as described above. The benzoate base (XVI) was obtained, b. p. 160-167° at 1 mm, a heavy, viscous oil which was at once converted into the hydrochloride.

Found %: C 78.03, 78.51; H 8.47, 8.79. $C_{22}H_{31}O_2N$. Calculated %: C 78.2; H 8.8.

The yield was 1.1 g of the hydrochloride of 1-n-butyl-1-phenyl-2-methyl-3-dimethylaminopropan -1-ol benzoate (XVI) with m. p. 103-105° (in sealed capillary) (from acetone).

Found %: N 3.67, 3.24. $C_{23}H_{32}O_2NCl$. Calculated %: N 3.59.

1-Isoamyl-1-phenyl-2-methyl-3-dimethylaminopropan -1-ol benzoate (XVII). 2.64 g of the amino alcohol (VII), 2.25 g of benzoyl chloride, and 10 ml of dry benzene was taken. The whole crystallized after 1 hour. The following day the mass was treated as described above. The result was 1.5 g of a very viscous liquid with b. p. 167-170° at 1 mm – the base (XVII), which could not be converted into the hydrochloride. In all cases an oil was formed which did not crystallize during a month.

0.5 g of the phosphate of 1-isoamyl-1-phenyl-2-methyl-3-dimethylaminopropan -1-ol benzoate (XVII) with m. p. 142-144° (from acetone and ether) was obtained.

Found %: C 50.97; H 7.05; N 2.24. $C_{24}H_{33}O_2N \cdot 2H_3PO_4$. * Calculated %: C 51.2; H 6.95; N 2.48.

SUMMARY

Several new secondary and tertiary alkyl aryl amino alcohols (1-phenyl-2-methyl-3-dimethylamino-propan -1-ols) and their esters were synthesized for pharmacological study.

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The Moscow Institute of Fine Chemical Technology

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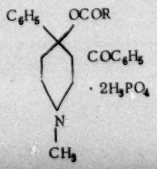
* As an example of such a phosphate we cite



[7].

THE REACTION OF ADIPIC ACID AND AMMONIA

E. N. Zil'berman

In the preparation of nitriles from monobasic carboxylic acids and ammonia, ammonium salts and amides are formed as intermediate products. The reversibility of amidation reactions was established as early as 1884 by N. A. Menshutkin [1]. Later it was found that the dehydration of amides to form nitriles is also reversible [2].

In the present work the mechanism of the reaction for the preparation of adiponitrile from adipic acid and ammonia was studied. It is usually assumed in the literature [3] that the formation of dinitriles from dibasic acids takes place through the intermediate formation of neutral ammonium salts and diamides. According to this scheme 2 molecules of water are split off at once during the reaction. However, it appeared to us more probable that each consecutive transformation is the result of the removal of only one molecule of water:

$$H_4NOOC(CH_2)_4COONH_4 \;(I) \rightleftharpoons H_4NOOC(CH_2)_4CONH_2 \;(II) \rightleftharpoons$$

$$\rightleftharpoons H_2NOC(CH_2)_4CONH_2 \;(III) \rightleftharpoons H_4NOOC(CH_2)_4CN \;(IV) \rightleftharpoons H_2NOC(CH_2)_4CN \;(V) \rightleftharpoons NC(CH_2)_4CN. \;(VI)$$

This means that in addition to ammonium adipate (I) and adipamide (III), the intermediate reaction products may also include compounds with two different functional groups: ammonium adipamate (II), ammonium δ-cyanovalerate (IV), and δ-cyanovaleramide (V).

For confirmation of this reaction mechanism we studied the composition of the crude product obtained by the reaction between adipic acid and ammonia. According to the literature, only (III) and (V), of all the probable intermediate products, were found in crude adiponitrile (VI) [4].

Identification of the substances isolated from the reaction mixture was made much easier because earlier a method was developed jointly with Z. D. Skorikova [5] for the quantitative determination of ammonium, amide, and nitrile groups when present together in adipic acid derivatives.

The reaction between adipic acid and ammonium was effected in the vapor phase in a continuous apparatus in the presence of boron phosphate as catalyst [6]. When the synthesis was carried out in the optimum conditions, the product contained 80% and over of the theoretical amount of adiponitrile. The reaction products did not contain any ammonia nitrogen, and the amide nitrogen did not exceed 1-2% of the total nitrogen. By a considerable increase of the load on the catalyst a reaction mixture was obtained which contained, in addition to nitrile nitrogen, also appreciable amounts of amide and ammonium nitrogen. The product was, however, mainly adiponitrile. In addition, (V), (III), adipic, adipamic, and δ-cyanovaleric acid were isolated. The ammonium salts of the last two substances were not obtained pure, as they partly dissociate in the air to give the original acids and ammonia. Thus, substances were isolated and identified, the presence of which in the reaction products

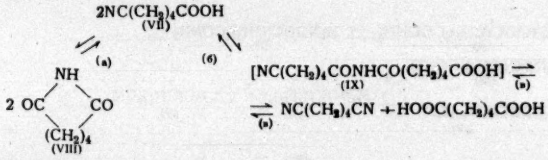
confirms the mechanism proposed above for the preparation of adiponitrile from adipic acid.

During the distillation of δ-cyanovaleric acid it was observed that it is unstable at high temperatures. This led us to develop a method for the synthesis of this acid and to study the products obtained when it is heated. In earlier papers [7-9], the constants for δ-cyanovaleric acid are almost entirely lacking. On the basis of molecular weight determinations it is reported that the acid apparently exists in the free state as the dimer, and on heating it forms a polymer.

In our method for the preparation of δ-cyanovaleric acid the starting material was δ-cyanovaleramide. The basis of the method is that amide derivatives of adipic acid are quantitatively saponified to the acids when boiled with dilute sulfuric acid, while nitrile derivatives of the same acid are almost entirely stable in the same conditions. The yield of δ-cyanovaleric acid reaches 80%. The molecular weight, molar refraction, and the other constants of the acid obtained indicate that it exists in the free state as the monomer.

Carothers [10] showed that there are two possible reaction directions in the homopolycondensation of amino and hydroxy carboxylic acids: one leads to the formation of linear polymers, and the other, to ring formation. The direction taken by the reaction largely depends on the number of atoms forming the unit monomer molecule. With six and seven-membered units both cyclization and formation of linear macromolecules takes place. Knunyants, Rogovin and co-workers [11] showed that the polymerization of ε-caprolactam obeys the same laws: the reaction product always contains a definite amount of monomer.

It was of interest to study the effect of heat on δ-cyanovaleric acid (VII), the molecular unit of which contains 7 atoms. It was assumed that heating results in a reaction between the acid and nitrile groups with the formation of secondary amides [12]. By analogy with amino and hydroxy acids, and on the basis of data concerning the formation of a five-membered cyclic amide in a similar instance [13], the reaction might be expected to proceed in either of two directions: a) in the direction of adipimide formation (VIII), and b) with the formation of a linear compound, in the first instance N-(δ-cyanovaleryl)-adipamic acid (IX):



Adipimide, adiponitrile, adipic acid, and also the unreacted original acid, were isolated and identified from the mixture of substances obtained by the heating of δ-cyanovaleric acid in a vacuum or in sealed tubes. No N-(δ-cyanovaleryl)-adipamic acid was isolated from the product. However, the presence of adipic acid and adiponitrile in the reaction products indicates that this compound is nevertheless apparently formed, but then immediately decomposes according to Reaction (c).

The proposed scheme for the reaction mechanism is also confirmed by the presence of adipimide and δ-cyanovaleric acid in the product obtained when equimolecular amounts of adipic acid and its dinitrils are heated together.

EXPERIMENTAL

(Jointly with K. M. Laputina)

The determination of the amide and nitrile groups was carried out by the method developed previously [5]. In this method the possibility of the presence of secondary amide nitrogen is not taken into account. It was found that secondary amide groups are saponified by acids with rather more difficulty than primary amide groups, and easily, as to be expected, by alkalies; therefore, the data given below on the amide nitrogen content must be regarded as provisional values.

For the preparation of the catalyst, 111 g of boric acid was added at room temperature and with thorough

stirring to a porcelain basin containing 231 g of 85% orthophosphoric acid. The homogeneous mixture was kept twenty-four hours at room temperature and dried 18 hours at 100-110°. The resultant dry mass was broken into 3-6 mm pieces. Before being used for the synthesis, the catalyst was additionally dried 4 hours in the contact tube at 350°.

The reaction between adipic acid and ammonia was carried out in a special steel contact tube (1000 mm long, 32 mm diameter) heated in an electric furnace. 300 ml of the catalyst was placed in the tube, which was fed with ammonia heated to 300° and, from a buret, with a solution of 150 g of adipic acid (m. p. 151-152°) in 90 ml of ammoniacal water (d_4^{20} 0.945). The feed rate was 220 g of ammonia and 105 g of adipic acid per hour. The temperature in the reaction zone was 350-360°. The reaction products entered a receiver, in which most of the organic substances and zone water was condensed. The gas-vapor mixture then passed through a water bulb condenser, a receiver, and two traps cooled by water.

The products of the reaction between adipic acid and ammonia, consisting of 323 g of an oily layer and 1122 g of an aqueous layer, were extracted with benzene. After removal of the benzene, 2.3 g of cyclopentanone (m. p. of oxime 56°) and 331 g of adiponitrile with the constants of the pure substance [14] were obtained. At 175-195° (3 mm), 6.9 g of δ-cyanovaleramide with m. p. 62° (from a mixture of ethyl ether and ethyl acetate) was collected.

Found %: N (nitrile) 11.22; N (amide) 10.78. $C_6H_{10}ON_2$. Calculated %: N (nitrile) 11.11; N (amide) 11.11.

The aqueous residues from the benzene extraction were evaporated at 100-110°. The yield was 172 g of a product part of which crystallized. The liquid (A) was decanted from the solid portion (B). The product A (81 g), which was δ-cyanovaleric acid, was distilled at 183-188° (10 mm). 100 ml of methanol was added to 49 g of the solid (B). The mixture was boiled 10 minutes, cooled, and 18 g of a solid (C) was separated from the liquid (D). A stream of ammonia was passed through (D) on cooling. 7.5 g of white crystals was deposited. These were dissolved in 100 ml of water, which was then cooled and acidified with concentrated sulfuric acid. Adipic acid separated out on standing (equivalent 75.1, m. p. 151°). 15 g of the product C was washed on the filter with 5% ammonium carbonate solution (solution E was formed) and water. The product which remained on the filter had m. p. 224°, and gave no melting point depression with known adipamide [15].

Found %: N (amide) 19.15. $C_6H_{12}O_2N_2$. Calculated %: N 19.39.

The solution E was cooled and acidified with concentrated sulfuric acid. White crystals were deposited on standing, with m. p. 146-151° and with a content of 9.0% amide nitrogen (calculated for adipamic acid, 9.64%). A sample mixed with pure adipamic acid (m. p. 158°) melted at 153°.

Pure δ-cyanovaleric acid was prepared as follows: a solution of 30 g of δ-cyanovaleramide (m. p. 62-64°) in 400 ml of 12% sulfuric acid was boiled 15 minutes and then treated with cyclohexanone. The extract was washed with small portions of 20% barium chloride solution until precipitation of barium sulfate ceased, and distilled under vacuum. After removal of the cyclohaxanone, two fractions were collected: first fraction b. p. 116-130° (2 mm), 2.5 g; second fraction 133-137° (2 mm), 24 g. The first fraction, after treatment with sodium carbonate solution, entirely corresponded to adiponitrile by its boiling point (119° at 2 mm) and other constants. The second fraction (δ-cyanovaleric acid) is a colorless or slightly pink liquid.

B. p. 158-160° (5 mm), solidifies at 12.7°, n_D^{20} 1.4481, d_4^{20} 1.0879, MR_D 31.21; Calc. 31.26.

Found %: N (nitrile) 10.90, 11.04; N (amide) 0.0, 0.2. Equiv. 127.6, 128.0; M (in phenol) 129.3, 126.1. $C_6H_9O_2N$. Calculated %: N (total and nitrile) 11.02; N (amide) 0.0 equiv. and M 127.14.

δ-Cyanovaleric acid is soluble in water, cyclohexanone, methylene chloride, and adiponitrile.

15 g of δ-cyanovaleric acid was heated slowly during 4 hours from 160 to 230° (35 mm), and a further 2 hours at 230° (20 mm). 13.6 g of solid oily brown product was obtained, 10 g of which was treated with benzene. The residue (4.5 g) was washed with 20 ml of 5% soda solution. The part of the residue which did not dissolve in the soda solution (3 g) had m. p. 170-172° (from water). The yield after recrystallization was negligible. The adipimide obtained is insoluble in benzene and nitrobenzene, and dissolves readily in phenol and alkalies.

Found %: C 55.91, 56.48; H 7.27, 7.00; N (Kjeldahl) 10.70, 10.79; N (nitrile) 11.10 10.98; N (amide) 8.2, 9.0. Equiv. 130.8; M (in phenol) 123.3. $C_6H_9O_2N$. Calculated %: C 56.68; H 7.13; N (total and amide) 11.02. Equiv. and M 127.14.

0.3 g of the imide was boiled 15 minutes with 5 ml of 25% sulfuric acid. About 0.15 g of adipic acid was deposited after cooling. Equivalent: found, 77.6; calculated, 78.07. No depression of melting point was found in a sample mixed with pure adipic acid.

The benzene extract was distilled. Two fractions were obtained; the first fraction b. p. 135-145° (5 mm) with 23.0% nitrile nitrogen content, which corresponds to adiponitrile; the second fraction with b. p. 158-167° (5 mm), equivalent 149, nitrile content 12.3%, which corresponds to δ-cyanovaleric acid.

To isolate adipic acid, 7 g of the product obtained by the heating of δ-cyanovaleric acid in the conditions described above was boiled several minutes with 40 ml of benzene. Adipic acid (m. p. 146°, equiv. 78.0) was obtained when the hot benzene solution was cooled.

15 g of adiponitrile and 20.2 g of adipic acid was heated 1 hour to 220° (20 mm), and then 4 hours at 220-230° (20 mm). The product was washed with benzene, cyclohexanone, and water. The residue (4.9 g) had m. p. 170° (from water). Adiponitrile and δ-cyanovaleric acid were isolated from the benzene extract.

SUMMARY

1. It was shown that, in the preparation of adiponitrile from adipic acid and ammonia, ammonium adipamate, adipamide, ammonium δ-cyanovalerate, and δ-cyanovaleramide are formed as intermediate products.

2. A method for the synthesis of δ-cyanovaleric acid was developed, based on the partial hydrolysis of δ-cyanovaleramide in the presence of sulfuric acid.

3. It is established that, when δ-cyanovaleric acid is heated, a reaction occurs between the nitrile and acid groups both from different molecules and within the same molecule. Accordingly, two reactions occur: a) formation of adipic acid and adiponitrile, and b) ring closure with the formation of adipimide. Both are equilibrium reactions and proceed easily in the opposite direction.

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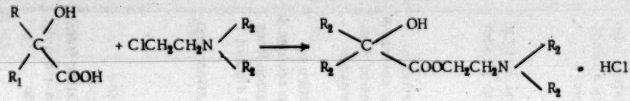
ESTERS OF AMINO ALCOHOLS AND DISUBSTITUTED GLYCOLIC ACIDS

N. V. Khromov-Borisov and N. A. Zakharova

Many esters of amino alcohols and disubstituted glycolic acids have a spasmolytic action. A series of such esters is described in the present paper. The acids used were benzilic, furylic, benzofurylic, anisylic, benzoanisylic, and diphenyleneglycolic. The esterification of such α-hydroxy acids is best effected by their reaction with an amino alcohol chlorohydrin (dialkyl aminochloroethane) in an organic solvent, the hydrochloride of the corresponding ester being formed:



The hydroxy acids were prepared from the corresponding aromatic aldehydes. The benzoin condensation of the aldehydes was carried out in most instances by means of the methods described in the literature: benzoin [1], anisoin [2], banzoanisoin [3]; some modifications were only introduced in the preparation of furoin [4] and benzofuroin [5]. In the preparation of benzofurylic and benzoanisylic acids the mixture of benzoins after purification was at once oxidized to a mixture of benzils [6], the separation of which proved less difficult.

The α-diketones were converted into the corresponding disubstituted glycolic acids by the benzil rearrangement [7, 2, 8, 5, 9].

By the esterification of all the above acids, with the exception of furylic (because of the extreme instability of the acid itself) and of diphenyleneglycolic, both by dimethylamino- and by diethyleminochloroethane, we obtained a whole series of disubstituted glycolic ester hydrochlorides, most of which are not described in the literature, details of which are shown in Table 1.

The esterification of diphenyleneglycolic acid led to unexpected results. The literature contains indications [10] that when this acid reacts with diethylaminochloroethane in boiling isopropyl alcohol, the ester hydrochloride with b. p. 204° is formed. We carried out this reaction in a medium of chlorobenzene, and also in milder conditions, in boiling toluene. Two products were isolated instead of the expected hydrochloride. One of these was the bis-hydrochloride of diethylaminoethoxydiphenyleneacetic acid diethylaminoethyl ester (I), and the other was diphenylene carbinol (II). Thus, both the hydroxyl of the carboxyl group and the alcohol hydroxyl in diphenyleneglycolic acid were esterified. At the same time partial decarboxylation of the acid with the formation of fluorenol took place. The reaction may be represented as follows:

TABLE 1

[R' = $CH_2CH_2N(CH_3)_2$; R" = $CH_2CH_2N(C_2H_5)_2$]

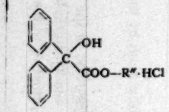
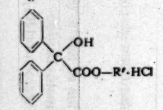
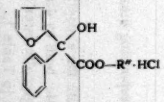
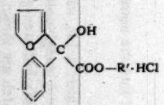
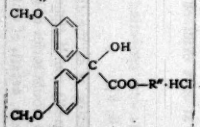
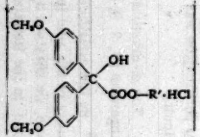
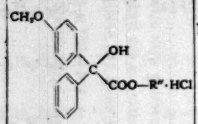
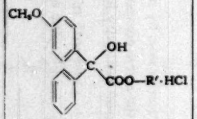
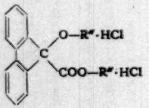
Serial No.	Name of Compound	Formula	Melting Point	Method of Purification	Yield (in %)	Found (in %)				Calculated (in %)			
						C	H	N	Cl	C	H	N	Cl
1	Diethylaminoethyl benzilate hydrochloride		174—175°	Crystallization from anhydrous alcohol or acetone	81.6	—	—	—	—	—	—	—	—
2	Dimethylaminoethyl benzilate hydrochloride		180	Crystallization from anhydrous alcohol	69.3	—	—	—	10.10, 10.24	—	—	—	10.56
3	Diethylaminoethyl benzofurylate hydrochloride *		143—145	Reprecipitation by ether from acetone & crystallization from alcohol-benzene mixture	76.9	60.79, 60.89	6.69, 7.01	3.92	10.20, 10.12	61.10	6.84	3.96	10.02
4	Dimethylaminoethyl benzofurylate hydrochloride *		177.5—178	Reprecipitation by ether from acetone & crystallization from anhydrous alcohol	66.1	—	—	4.38, 4.23	10.88, 10.83	—	—	4.30	10.88
5	Diethylaminoethyl anisylate hydrochloride		167**	Crystallization from acetone	87.1	62.60, 62.32	6.82, 7.00	3.40	8.36, 8.39	62.33	7.13	3.30	8.36
6	Dimethylaminoethyl anisylate hydrochloride		191—192	Crystallization from anhydrous alcohol or acetone	63.4	—	—	—	9.20, 9.24	—	—	—	8.96

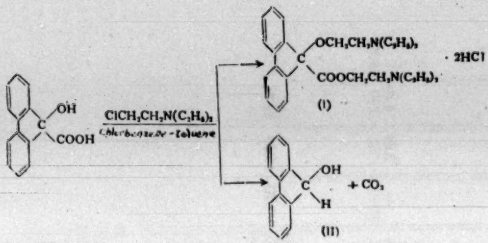
TABLE 1 (Continued)

Serial No.	Name of Compound	Formula	Melting Point	Method of Purification	Yield (in %)	Found (in %)				Calculated (in %)			
						C	H	N	Cl	C	H	N	Cl
7	Diethylaminoethyl benzoanisylate hydrochloride		155—156***	Crystallization from anhydrous alcohol	96.2	—	—	3.57, 3.79	8.96, 8.93	—	—	3.56	9.00
8	Dimethylaminoethyl benzoanisylate hydrochloride *		185—187	*	63.9	—	—	3.94, 3.70	9.98, 10.00	—	—	3.83	9.69
9	Diethylaminoethyl diethylaminoethoxy-diphenyleneacetate (bis) hydrochloride *		190—191	*	35.5	62.99, 63.12	7.62, 7.71	5.42, 5.61	14.79, 14.70	62.77	7.70	5.63	14.26

* Prepared for the first time.

** According to literature data [16], m. p. 157°, other sources [10] give 172°.

*** According to literature data [17] m. p. 169-171°.

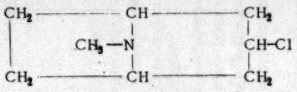


The composition of the ether-ester (I) was confirmed by elementary analysis. Fluorenol was identified by oxidation to diphenylene ketone [11] and also by conversion to the acetyl derivative [12].

Diphenylglycolic (benzilic) acid and diphenyleneglycolic acid differ from each other only by the presence of a bond between the benzene rings in the latter. The formation of this bond favors easier etherification of the alcohol hydroxyl, and also easier removal of carbon dioxide from the carboxyl.

A similar reaction cannot be effected with dimethylaminochloroethane, as the latter is converted into a tetramethylpiperazine salt in these conditions.

For the preparation of esters of disubstituted glycolic acids and tropine, we synthesized 3-chlorotropane (III) which agreed in its properties with



(III)

3-chlorotropane prepared by the Polanovskis [13] from belladonine. However, these authors erroneously ascribed the empirical formula $C_8H_{14}ONCl$ to it. In reality 3-chlorotropane has the structural Formula (III) and contains no oxygen.

Experiments with 3-chlorotropane showed that it does not form esters by reacting with disubstituted glycolic acids. These acids form salts with 3-chlorotropane which have the same composition as the hydrochlorides of the corresponding esters. In contrast to the latter they dissolve with difficulty in water and easily in alkalies.

3-Chlorotropane reacts with diphenylacetic acid similarly: a salt with m. p. 124-125° is formed. The action of diphenylacetyl chloride on tropine gives diphenylacetic acid tropine ester hydrochloride, which has m. p. 212-213° [14, 15].

Details of the tropine derivatives are shown in Table 2.

EXPERIMENTAL

Condensation of dialkylaminochloroethane with disubstituted glycolic acids. To a solution of 0.02 mole of the freshly distilled dialkylaminochloroethane base in 20 ml of chlorobenzene or toluene, 0.02 mole of the acid was added and the mixture heated on a glycerol bath between 2.5 and 4 hours at 110-120° bath temperature. The precipitate of the ester hydrochloride was washed with anhydrous ether and purified by crystallization or reprecipitation. The results are shown in Table 1.

Reaction of diphenyleneglycolic acid with diethylaminochloroethane. To 2.47 g of the freshly distilled diethylaminochloroethane base in 16 ml of chlorobenzene 4.12 g of diphenyleneglycolic acid was added and

TABLE 2

Serial No.	Name of compound	Empirical formula	Melting Point	Method of Purification	Yield	Found (in %)		Calculated (in %)	
						N	Cl	N	Cl
1	Salt of 3-chlorotropane and benzilic acid	$C_{22}H_{26}O_3NCl$	141–142°	From benzene	98.9	3.58, 3.59	9.08, 9.10	3.61	9.14
2	Salt of 3-chlorotropane and benzoanisylic acid	$C_{23}H_{28}O_4NCl$	167.5–168	From anhydrous benzene	Quantitative	3.45, 3.55	8.26, 8.28	3.35	8.48
3	Salt of 3-chlorotropane and diphenylacetic acid	$C_{28}H_{30}O_2NCl$	124–125	From a mixture of ligroine and benzene (3:1)	78–88.2	3.86, 3.89	9.52, 9.59	3.77	9.53
4	Tropine diphenyl-acetate hydrochloride	$C_{28}H_{30}O_2NCl$	212–213	Reprecipitation (see Experimental Section)	57.8	–	9.45 9.41	–	9.53

the mixture heated 4 hours at 120–125°. The precipitate was washed with chlorobenzene and boiled with ether. The residue (3.2 g, 35.5%) was diethylaminoethyl diethylaminoethoxy-diphenyleneacetate bis-hydrochloride, m. p. 190–191°. Fluorenol (1.45 g) obtained after removal of the chlorobenzene and the ether used for washing had m. p. 153–154° (from aqueous alcohol); oxidation by means of chromic anhydride gave yellow needles of fluorenone with m. p. 67–68° [11], and acetylation gave white needles of 9-acetoxyfluorene with m. p. 69–70° [12].

The reaction of 2.6 g of diphenyleneglycolic acid with 1.2 g of freshly distilled dimethylaminochloroethane in the conditions of the preceding experiment yielded fluorenol (1.71 g) and tetramethylpiperazine (bis) hydrochloride (1.09 g) with m. p. above 316° (from aqueous alcohol).

Found %: Cl 32.49, 32.78. $C_8H_{20}N_2Cl_2$. Calculated %: Cl 32.96.

Preparation of 3-chlorotropane. 14.1 g of tropine in 40 ml of dry dichloroethane was cooled to a temperature of minus 10–12° and 14.15 g thionyl chloride in 15 ml of dichloroethane was added during 5 hours with constant stirring. The mixture was then slowly heated and boiled 2.5 hours. The precipitate of 3-chlorotropane hydrochloride (8.52 g) had m. p. 234° (from anhydrous alcohol). The salt was dissolved in 30 ml of 25% caustic soda, the oil was extracted with ether, and the extracts were washed with water and dried by potash. The pale yellow oil which remained after removal of ether was distilled under vacuum, and 5.19 g with b. p. 84–85° at 9 mm was collected. The picrate had m. p. 215–216° (from alcohol).

A small amount of tropidine, b. p. 39–42° at 8 mm, and with a picrate m. p. 285° [18], was obtained from the used dichloroethane.

Reaction of 3-chlorotropane with benzilic, benzoanisylic and diphenylacetic acids. 0.005 mole of the acid was suspended in 10 ml of anhydrous toluene, and 0.8 g (0.005 mole) of the freshly distilled 3-chlorotropane base in 5 ml of anhydrous toluene was added dropwise with stirring; the acid dissolved, but white crystals soon began to form and the mass thickened. After half an hour the precipitate was filtered off and crystallized from the appropriate solvent. The substances dissolve with difficulty in water and acids, and better in alkali solutions. No ionic chlorine could be detected in the aqueous solutions. Quantitative hydrolysis of the chlorine was effected by boiling with 10% soda solution during 1 hour. The results are shown in Table 2.

Preparation of tropine diphenylacetate hydrochloride [14, 15]. Diphenylacetic acid was prepared by the method given in the literature [19]. Its acid chloride, m. p. 53–54°, was prepared by heating the acid with thionyl chloride [20]. 6.9 g of diphenylacetyl chloride was dissolved in 15 ml of anhydrous toluene, and 5.1 g (20% excess) of thoroughly dried tropine in 15 ml of anhydrous toluene was added with stirring and cooling. The mixture was heated 5 hours at 120–125°. The precipitate (9.82 g) was washed with ligroine and anhydrous ether. For purification, the substance was dissolved in 80 ml of 20% caustic soda and the base was extracted with ether. The extracts were washed with water, dried with potash, boiled with charcoal, and filtered. Anhydrous solution of hydrogen chloride in ether-alcohol mixture was added to the colorless ether solution. The precipitate (6.45 g) was tropine diphenylacetate hydrochloride, m. p. 212–213°.

SUMMARY

1. A series of hydrochlorides of disubstituted glycolic acid dialkylaminoethyl esters has been prepared.

2. It is shown that diphenyleneglycolic acid, in contrast to the other disubstituted glycolic acids, reacts with diethylaminochloroethane both at the acid and at the alcohol hydroxyl. Simultaneously part of the acid is converted into fluorenol.

3. A study of the reaction between 3-chlorotropane and benzylic, benzoanisylic, and diphenylacetic acids showed that 3-chlorotropane does not form tropine esters of these acids; only salt formation occurs.

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SYNTHESIS AND PROPERTIES OF SOME BENZIMIDAZOLE DERIVATIVES REACTIONS OF o-PHENYLENEDIAMINE WITH SOME CARBOXYLIC ACIDS

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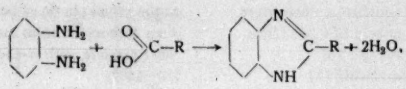
The presence of hydrogen ions in the reaction medium during the reaction between o-diamines and carboxylic acids,



on the one hand, hinders hydrolysis of the o-diamine hydrochloride, and on the other, favors polarization of the double bond and the formation of the carboxylic acid cation [1, 2]:

The relationship between amine basicity, hydrolysis of their salts, and the capacity for forming imidazole derivatives has been studied in considerable detail [1-3]. The effect of hydrochloric acid on the reactivity of carboxylic acid has been studied less. It is known, for example, that acetic acid ($K = 1.8 \cdot 10^{-5}$) in the presence of 4 N hydrochloric acid reacts very readily with o-phenylenediamine to form 2-methylbenzimidazole, while benzoic acid ($K = 6.8 \cdot 10^{-5}$) does not condense with it in under these conditions [4]. The reaction between benzoic acid and o-diamines in the presence of hydrochloric acid only proceeds under pressure [1, 2]. The activity of benzoic acid increases with increase of hydrogen chloride concentration in the reaction mixture to 20–25% [1, 2]. Further increase of the concentration decreases the yield of 2-phenyl derivatives of benzimidazole [1, 2]. The reactivity of benzoic acid, as Table 1 shows, is much less in the presence of 35% hydrochloric acid than the reactivity of acetic acid in the same conditions.

On the basis of these data and of earlier theoretical considerations [1, 2] it might be expected that the higher is the degree of dissociation of the carboxylic acid, the higher is the hydrogen chloride concentration needed to reach maximum activity.

The results of our work do not contradict this, but they show that the specific structural features of the carboxylic acids should also be considered. For example, a study of the behavior of a number of carboxylic acids when heated with o-phenylenediamine in the presence of 35% hydrochloric acid shows that their reactivity is largely determined by the structure of the radical linked to the carbonyl group (Table 1). For example, aromatic acids (benzoic, p-chlorobenzoic) in these conditions condense far less readily with o-phenylenediamine than do the fatty or alkyl aromatic acids. The activity of acetic acid is rather lower than the activity of hydrocinnamic and phenylacetic acid. The reactivity of the latter is close to the reactivity of formic and mandelic acid (Table 1 and 2).

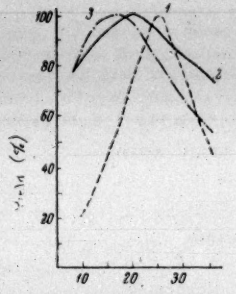


Fig. 1. Effect of hydrochloric acid concentration on the yields (in %) of benzimidazole derivatives when carboxylic acids are heated in tubes 1 hour with o-phenylenediamine at 160–170°.
1) Yield of 2-phenylbenzimidazole [1],
2) yield of 2-benzylbenzimidazole
3) yield of 2-methylbenzimidazole.

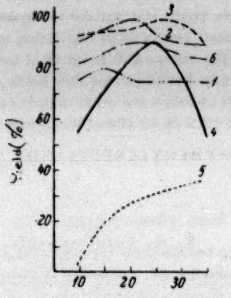


Fig. 2. Effect of hydrochloric acid concentration on the yields (in %) of benzimidazole derivatives when carboxylic acids are heated 5 hours in tubes under pressure with o-phenylenediamine at 150–160°.
1) Yield of 2-methylbenzimidazole,
2) yield of 2-benzimidazole,
3) yield of 2-(p-hydroxybenzyl)-benzimidazole,
4) yield of 2-phenylbenzimidazole,
5) yield of 2-(p-aminophenyl)-benzimidazole,
6) yield of 2-(m-aminophenyl)-benzimidazole.

Apparently the structure of the radical influences not only the degree of dissociation of the carboxylic acids, but also the degree of polarization of the double bond and the degree of saturation of the electron void of the carboxyl group carbon, and consequently the reactivity of the carboxylic acid.

Interesting results were obtained in a study of the effect of hydrochloric acid concentration on the activity of some carboxylic acids. The reactivity of most carboxylic acids grows with increasing concentration of hydrogen chloride in the reaction mixture, but only to a certain limit, after which it falls (Fig. 1, 2). It was found that for a number of these acids the optimum concentration of hydrochloric acid increases with increasing degree of dissociation (Table 1). At low hydrochloric acid concentrations the reactivity of aromatic acids (Fig. 2, Table 1) is much less than the reactivity of fatty and alkyl aromatic acids. The activity of the latter is fairly high (the yields of benzimidazole derivatives were about 80%) even in the presence of 10% of hydrochloric acid (Fig. 2, Table 2); therefore a further increase of hydrochloric acid concentration has a less pronounced influence on the yields of benzimidazole derivatives than when aromatic acids are used (Fig. 1, 2). p-Nitrobenzoic and anisic* acids decompose in the conditions of the experiment. The behavior of amino derivatives of benzoic acid (Table 2) is peculiar. Their reactivity increases with rise of their dissociation constant. Anthranilic acid does not react with o-phenylenediamine in the given experimental conditions.

* 2-(p-Methoxyphenyl)-benzimidazole was obtained in a low yield by the fusion of o-phenylenediamine with anisic acid.

TABLE 1

Reactivity of Some Carboxylic Acids in Their Reaction with o-Phenylenediamine

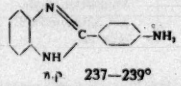
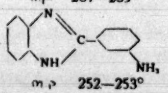
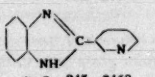
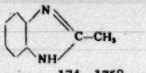
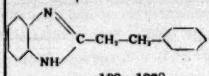
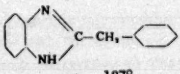
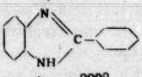
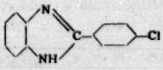
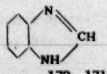
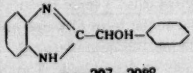
Serial No.	Acid	Dissociation constant $K \cdot 10^5$	Yield of benzimidazole derivative (in %) in the presence of 35 %		Optimum HCl concentration for maximum yield (in %)	Formula and m. p. of benzimidazole derivative
			7 hours at 160-170°	2 hours at 140-150°		
1	Anthranilic	1.07	0	—	—	Not formed in these conditions
2	p-Aminobenzoic	1.21	38	—	35	 m.p. 237—239°
3	m-Aminobenzoic	1.63	83	—	20	 m.p. 252—253°
4	Nicotinic	1.4	84	65	—	 m.p. 245—246°
5	Acetic	1.8	88	55	15—20	 m.p. 174—175°
6	Hydrocinnamic	2.3	98	85	15—20	 m.p. 189—190°
7	Phenylacetic	6.0	about 100	85	20	 m.p. 187°
8	Benzoic	6.8	50	26	25	 m.p. 290°
9	p-Chlorobenzoic	10.4	40	35	30	
10	Formic	17.7	80	—	—	 m.p. 170—171°
11	Mandelic	43	100	87	25—30	 m.p. 207—208°

TABLE 2

Serial No.	Acid	Yield of benzimidazole derivative (in %) at different hydrochloric acid concentrations					
		10	15	20	25	30	35
1	p-Aminobenzoic	2—5	20—25	28—30	30—33	33—35	38—40
2	m-Aminobenzoic	82	85	90	89	84	84
3	Anthranilic	CONDENSATION DOES NOT OCCUR					
4	Benzoic	55	—	83	90	80	53
5	Nicotinic	69	74	80	—	80	74
6	Mandelic	93	95	95	98	98	88
7	Phenylacetic	90—92	95	99	92	90	89
8	Hydrocinnamic	86	89	88	82	60	50
9	p-Chlorobenzoic	53	60	67	68	70	40
10	Acetic	75	78—80	75	—	75	—

p-Aminobenzoic acid reacts only to the extent of 40%. m-Aminobenzoic acid reacts with o-phenylenediamine very readily (to 80-85%). Its reactivity approaches that of the alkyl aromatic acids (Fig. 1, 2). The optimum concentration of hydrogen chloride is rather higher for p-aminobenzoic acid than for m-aminobenzoic acid (Table 1).

Such behavior of these acids is apparently associated with the fact that in the experimental conditions used the amino group loses its basic properties owing to salt formation and becomes an electron acceptor instead of an electron donor substituent.

EXPERIMENTAL

1. Reaction of o-phenylenediamine with some carboxylic acids. a) Equimolecular amounts (0.01 mole) of o-phenylenediamine and the carboxylic acid were heated with 10 ml of 35% hydrochloric acid 5-7 hours in tubes at 150-160°. The contents of the tubes were extracted with hot water and treated to a neutral reaction (by Congo Red) with aqueous ammonia solution. The precipitate was filtered off, washed with cold water, and dried to constant weight. The results are shown in Table 1.

b) Equimolecular amounts (0.01 mole) of o-phenylenediamine and the carboxylic acid were heated 5 hours under pressure at 150-160° with different concentrations of hydrochloric acid. Data on the yields of benzamidazole derivatives are shown in Table 2 (Fig. 2).

2. Fusion of o-phenylenediamine with anisic acid. A mixture of equimolecular amounts of o-phenylenediamine and anisic acid was heated 1 hour on an air bath to 180°. The melt was cooled and dissolved in alcohol, and the alcoholic solution was carefully poured into aqueous (10%) ammonia. The reaction product was deposited in the form of a paste, which congealed on standing several days. Purification of the 2-(p-methoxyphenyl)-benzimidazole was effected by crystallization from alcohol. 2-(p-Methoxyphenyl)-benzimidazole consisted of white leaflets, m. p. 263-270°.

Found %: N 12.4. $C_{14}H_{12}N_2$. Calculated %: N 12.5.

No benzimidazole derivatives are obtained by the reaction of o-phenylenediamine with anisic acid in the presence of 10, 20 and 35% hydrochloric acid on heating to 150-160°, as anisic acid decomposes during the experiment.

3. Properties of some benzimidazole derivatives. 2-(p-Aminophenyl)-benzimidazole (I). The base was isolated in the form of white leaflets (from alcohol) with m. p. 237-239°. In its properties the substance agreed with the literature data [5]. The benzimidazole (I) hydrochloride ($C_{12}H_{11}N_3 \cdot 2HCl$) is easily soluble in water and can be diazotized. The diazo solutions couple with Azotol A to form a red dye.

2-(m-Aminophenyl)-benzimidazole (II) melts at 252-253° after recrystallization from alcohol. In its melting point and properties the substance agrees with the literature data. The benzimidazole (II) hydrochloride was isolated in the form of white silky needles which decompose at 294-300° (yield ~ 88%). The benzimidazole

(II) (bis) hydrochloride is easily soluble in water, less easily in alcohol, and with difficulty in ether.

2-Benzylbenzimidazole (III). The benzylbenzimidazole base agreed in its properties with the literature data [1].

Benzylbenzimidazole hydrobromide. 5.0 g of the base (III) with m. p. 185-186° was dissolved in 40 ml of alcohol. The alcoholic solution of benzylbenzimidazole (III) was saturated with dry hydrogen bromide and diluted with double the volume of water. The yield of hydrobromide was 5.2 g (75%). Properties: snow-white plates with indistinct melting point. This salt is rather difficultly soluble in water, and relatively easily in alcohol and in alcohol-ether mixture.

SUMMARY

1. The reactivity of carboxylic acids in the reaction with o-phenylenediamine to form benzimidazole derivatives depends to a large extent on their structure. The reactivity of aromatic acids is lower than the reactivity of fatty and particularly of alkyl aromatic acids.

2. The reactivity of carboxylic acids depends to a large extent on the concentration of the hydrochloric acid used in the reaction. The optimum concentration of the latter rises with increasing degree of dissociation of the carboxylic acid.

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SYNTHESIS OF 2-FORMYLQUINUCLIDINE

M. V. Rubtsov and L. N. Yakhontov

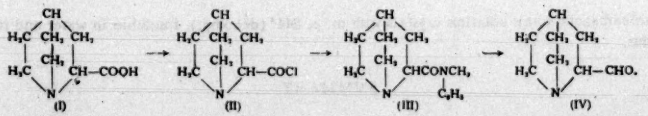
2-Formylquinuclidine is of considerable interest as a starting material for the preparation of various quinuclidine derivatives. This compound is not described in the literature.

We attempted to synthesize 2-formylquinuclidine by various methods from quinuclidine-2-carboxylic acid (I) [1]. The possibility of preparing 2-formylquinuclidine both by the decomposition of quinuclidine-2-carboxylic acid phenylsulfohydrazide, and by the oxidation of quinuclidyl-2 carbinol, was investigated.

The literature contains a description of the preparation of 4-formylpyridine thiosemicarbazone by the decomposition of isonicotinic acid phenylsulfohydrazide in the presence of thiosemicarbazide [2]. The use of this method for the decomposition of quinuclidine-2-carboxylic acid phenylsulfohydrazide did not yield 2-formylquinuclidine thiosemicarbazone.

It is known that selenium dioxide and lead tetraacetate have been used with success for the oxidation of a number of primary alcohols to the corresponding aldehydes [3]. However, the reaction of quinuclidyl-2 carbinol [4] with selenium dioxide gave selenoorganic compounds, while only traces of aldehyde were found upon oxidation of quinuclidyl-2 carbinol by lead tetraacetate.

The synthesis of 2-formylquinuclidine was achieved according to the following scheme:



Quinuclidine-2-carboxylic acid was converted into the acid chloride (II) by treatment with thionyl chloride. The reaction of the acid chloride with N-methylaniline gave the N-methylanilide of quinuclidine-2-carboxylic acid (III). Reduction of the N-methylanilide by means of the calculated amount of lithium aluminum hydride by Weygand's method [5] gave 2-formylquinuclidine (IV), which was purified through its bisulfite compound and characterized as the hydrochloride, picrate, phenylhydrazone, and semicarbazone.

EXPERIMENTAL

Quinuclidine-2-carboxylic acid N-methylanilide (III). A mixture of 4.44 g of quinuclidine-2-carboxylic acid hydrochloride and 45 ml of thionyl chloride was heated 14 hours at 60-65°. The precipitate dissolved completely in this time. The excess thionyl chloride was driven off under vacuum, and the remainder was removed by 3-fold addition of anhydrous benzene and its removal under vacuum. The resultant hydrochloride of quinuclidine-2-carboxylic acid chloride was added during 15 minutes with stirring to a solution of 8.1 g of N-methylaniline in

20 ml of anhydrous ether cooled to −2°. The stirring was continued another 2 hours, and the reaction mixture was then treated with 30 ml of 50% potash solution and extracted with ether. The ether solution was dried with potash. The ether and excess N-methylaniline were driven off under vacuum. The residue was distilled under vacuum at 0.6 mm. The yield was 4.8 g (85%) of quinuclidine-2-carboxylic acid N-methylanilide in the form of a colorless oily substance with b. p. 161-162°. On cooling the substance crystallized into colorless crystals with m. p. 95-96°, soluble in organic solvents, insoluble in water.

Found %: C 73.87, 74.06; H 7.95, 8.11; N 11.75. $C_{15}H_{20}ON_2$. Calculated %: C 73.78; H 8.19; N 11.47.

2-Formylquinuclidine (IV). To a solution of 2.7 g of quinuclidine-2-carboxylic acid N-methylanilide in 27 ml of anhydrous ether cooled to −5°, 0.21 g of lithium aluminum hydride was added during 15 minutes with stirring. The reaction mass was stirred 8 hours at the same temperature and treated with 0.4 ml of water. The precipitated lithium and aluminum hydroxides were filtered off and thoroughly washed with ether on the filter. The ether solution was treated with 2.5 ml of 40% sodium bisulfite solution. The bisulfite compound was filtered off, washed with alcohol, dried in a vacuum desiccator, and then decomposed by heating to the boil with 15 ml of saturated soda solution. The alkaline solution was cooled and the 2-formylquinuclidine which separated out was extracted with ether; the ether solution was dried with potash and divided into two equal portions. One portion, after removal of the ether, was distilled under vacuum at 0.4 mm. 0.3 g of a fraction with b. p. 80-82° was collected in the form of a colorless oily substance with a specific smell. The substance dissolves easily in the usual organic solvents and with difficulty in water; it gives a red color with Schiff's reagent and forms a silver mirror with ammoniacal silver oxide solution, n_D^{20} 1.5296.

Found %: C 68.64, 68.92; H 9.36, 9.46; N 10.23. $C_8H_{13}ON$. Calculated %: C 69.06; H 9.35; N 10.07.

The hydrochloride forms colorless crystals, m. p. 228° (decomp.), easily soluble in water and alcohol, insoluble in ether and acetone.

The picrate forms pale yellow crystals, m. p. 218-219° (decomp.), soluble in alcohol, insoluble in ether.

The second half of the ether solution of 2-formylquinuclidine was treated with 0.6 g phenylhydrazine. 2-Formylquinuclidine phenylhydrazone separated out on standing in the form of colorless crystals with m. p. 147-148°. Yield 0.4 g (31% calculated on the original quinuclidine-2-carboxylic acid N-methylanilide). The substance is soluble in chloroform, alcohol, and benzene, and very slightly soluble in ether and water.

Found %: C 73.45, 73.36; H 8.36, 8.29; N 18.05. $C_{14}H_{19}N_3$. Calculated %: C 73.36; H 8.29; N 18.34.

The semicarbazone forms colorless crystals with m. p. 244° (decomp.), insoluble in water and in organic solvents.

SUMMARY

1. 2-Formylquinuclidine was synthesized from quinuclidine-2-carboxylic acid by reduction of quinuclidine-2-carboxylic acid N-methylanilide with lithium aluminum hydride.

2. It was shown that 2-formylquinuclidine is not formed by the oxidation of quinuclidyl-2 carbinol by selenium dioxide or lead tetraacetate, or by the decomposition of quinuclidine-2-carboxylic acid phenylsulfohydrazide.

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INVESTIGATIONS OF QUINONES

VI. PREPARATION OF CHLORO AND BROMOQUINONES BY THE OXIDATION OF CHLORO- AND BROMO- SUBSTITUTED HYDROQUINONES

A. N. Grinev and A. P. Terentyev

With the aim of finding a better method for the preparation of various quinones we tested a number of methods for the oxidation of hydroquinones. The best results were invariably obtained by the oxidation of hydroquinones by means of potassium bromate in an acid medium. This method was proposed in the literature by McCoy [1] only for the oxidation of hydroquinone to p-benzoquinone. We succeeded in the use of potassium bromate for the synthesis of a number of chloro- and bromo- substituted p-quinones. The oxidation of chloro and bromohydroquinones by potassium bromate was carried out in aqueous solution with the addition of small amounts of sulfuric acid at 60-75° and thorough stirring. When the reaction resulted in the formation of quinhydrones sparingly soluble in water (in the oxidation of 2, 5-dichlorohydroquinone, 2, 3-dichlorohydroquinone, and 2, 6-dibromohydroquinone), a little dioxane was added to the reaction mixture. In all the experiments, halogen-substituted quinones were obtained in yields over 85%.

EXPERIMENTAL

(With the participation of V. K. Lomova)

1) Chloro-p-benzoquinone. Chlorohydroquinone (30 g) prepared by the method developed by the present authors [2] was dissolved with warming in 180 ml of water, the solution was cooled to room temperature, and 15 ml of 1 N sulfuric acid and 12.6 g of potassium bromate in 120 ml of water was added. The solution was heated to 60-62° with vigorous mechanical stirring. The solution darkened at first, and then a dark red oily layer (quinone together with hydroquinone) separated out. After further stirring at the same temperature the oily layer became yellow. The solution was then cooled and the deposited crystals of the chloroquinone were filtered off, washed with ice-cold water and dried over calcium chloride in a vacuum desiccator. The yield was 23.7 g of the chloroquinone. A further 2.1 g of the chloroquinone was extracted from the mother liquor. The total yield was 87.5%. M. p. 56-57°, in agreement with the literature data [3].

2) 2, 5-Dichloroquinone. 6 g of 2, 5-dichlorohydroquinone (prepared by heating chloroquinone with concentrated hydrochloric acid [3]) was dissolved with warming in a mixture of 70 ml of water and 20 ml of dioxane. 2.5 ml of 1 N sulfuric acid and 2.1 g of potassium bromate in 20 ml of water was added to the solution. The solution was warmed to 70-75° with stirring; the dark red color of the aqueous layer disappeared and the quinone already began to be deposited from the hot solution in the form of fine pale yellow crystals. The reaction liquid was cooled, and the crystals were separated off, washed with water, and dried. The yield was 5.6 g (94%) of the quinone. M. p. 159-160° in agreement with the literature data [4].

Some other halogenated hydroquinones were oxidized in analogous conditions. The results of the oxidation are shown in the Table.

Serial No.	Original hydroquinone	Quinone formed	Yield (in %)	Melting Point	
				our data	literature data
	Chlorohydroquinone	Chloro-p-benzoquinone	87.5	56—57°	57° [3]
	2, 5-Dichlorohydroquinone	2, 5-Dichloroquinone	94	159—160	158.5 [4]
	Bromohydroquinone	Bromo-p-benzoquinone	90	55—56	55 [5]
	2, 3-Dichlorohydroquinone	2, 3-Dichloroquinone	84.5	99—100	100—101 [4]
	2, 6-Dibromohydroquinone	2, 6-Dibromoquinone	88	130—131	131 [6]

* Experiment performed in conditions of Experiment 1).

** Experiment performed in conditions of Experiment 2).

SUMMARY

A method has been developed for the oxidation of halogenated hydroquinones to the corresponding quinones by means of potassium bromate in acid solution. Chloro-p-benzoquinone, bromo-p-benzoquinone, 2, 5-dichloroquinone, 2, 3-dichloroquinone, and 2, 6-dibromoquinone were obtained in 85-95% yields.

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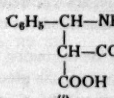
SYNTHESIS OF SOME β-N-ALKYLAMINO AND β-N-ARALKYLAMINO-β-PHENYLPROPIONIC ACIDS

V. M. Rodionov* and E. V. Yavorskaya

β-N-Methylamino-β-phenylpropionic acid was first obtained by V. M. Rodionov in a low yield by the heating of a mixture of benzaldehyde, malonic acid, and alcoholic methylamine solution. It was later synthesized by Evans and Johnson [2] in 41% yield by the heating of benzalmethylamine and malonic acid in an alcohol medium. In our previous study [1] this reaction between benzalmethylamine and malonic acid was carried out in benzene, which increased the yield of amino acid to 52-55%; the yield of cinnamic acid fell from 37 to 27-33%.

It is reported [2] that in the synthesis of β-N-methylamino-β-phenyl-propionic acid by the heating of the reagents in anhydrous alcohol a crystalline compound is rapidly formed, which gradually in the course of 3 hours passes into solution. These workers considered this intermediate reaction product to be the amino dicarboxylic acid (I) formed by the addition of malonic acid to benzalmethylamine.



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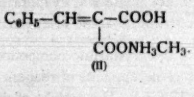

(II)

In the present study this intermediate reaction product [2] was isolated and investigated, and it was found that this compound is not β-phenyl-β-methylamino-α, α-ethanedicarboxylic acid, but the acid salt of benzalmalonic acid and methylamine (II), which has the same molecular composition.

The formation of acid ammonium salts of unsaturated dicarboxylic acids in the reaction for the preparation of amino acids by V. M. Rodionov's method was first described in the paper [3]. It is possible that the formation of acid salts of unsaturated dicarboxylic acids occurs as the result of the deamination of previously formed unstable amino dicarboxylic acids. When these salts are heated in anhydrous alcohol, decarboxylation occurs and the main reaction products are unsaturated monobasic acids and their salts.

A description is given below of the synthesis and properties of β-N-benzylamino-β-phenylpropionic acid, β-N-ethylamino-β-phenylpropionic acid, and β-N-propylamino-β-phenylpropionic acid. The intermediate reaction products—ethylammonium acid benzalmalonate and benzylammonium acid benzalmalonate—were isolated and are described.

EXPERIMENTAL

Preparation and study of methylammonium acid benzalmalonate. 4 g of benzalmethylamine, 3.2 g of malonic acid, and 20 ml of anhydrous alcohol were heated to the boil; a white crystalline precipitate was rapidly formed. 2-3 minutes after the start of the precipitation the flask was cooled in ice, and the precipitate was

* deceased

filtered off and washed with anhydrous ether. Yield 3 g (41.7%). M. p. 138° (decomp.).

The compound decolorized bromine water and reduced permanganate. Methylamine was evolved by the action of alkalies.

Found %: N 6.26, 6.40. $C_{11}H_{13}O_4N$. Calculated %: N 6.27.

1 g of the precipitate formed was treated with hydrochloric acid. 0.65 g of benzalmalonic acid with m. p. 190-191° (from water) was formed.

The acid salt of methylamine and benzalmalonic acid was prepared by the reaction of 0.5 g of methylamine with 3 g of benzalmalonic acid in alcohol. 3 g of the salt with m. p. 137° (decomp.) was precipitated. A sample mixed with the substance formed by the reaction between benzalmethylamine and malonic acid gave no melting point depression.

1 g of methylammonium acid benzalmalonate and 6 ml of anhydrous alcohol were boiled 4 hours. The precipitate gradually dissolved. The addition of anhydrous ether to the cooled alcohol solution did not cause the formation of an insoluble amino acid precipitate. Evaporation of the ether-alcohol solution and treatment of the residue with hydrochloric acid yielded 0.48 g (72.3%) of cinnamic acid.

Synthesis of β-N-benzylamino-β-phenylpropionic acid. a) 2 g of benzalbenzylamine, 1.1 g of malonic acid, and 10 ml of anhydrous alcohol was heated to the boil. After several minutes a crystalline precipitate was formed, which dissolved completely after 3 hours. The heating was continued a further 1.5 hours. Part of the alcohol was driven off, and the residue was treated with anhydrous ether. 2.1 g of crystals was gradually deposited. Treatment of a small portion of this precipitate with hydrochloric acid yielded cinnamic acid. Evidently the amino acid was precipitated by ether together with cinnamic acid salts. After recrystallization from 70% alcohol 0.34 g (13.1%) of β-N-benzylamino-β-phenylpropionic acid, m. p. 177°, was obtained. The compound is moderately soluble in hot water, easily in hot alcohol, and with difficulty in benzene.

Found %: N 5.53, 5.45. $C_{16}H_{17}O_2N$. Calculated %: N 5.45.

The ether-alcohol mother liquor was evaporated and the residue was treated with hydrochloric acid. 1.1 g (73%) of cinnamic acid was obtained after purification by dissolution in ether.

In order to investigate the crystalline compound formed at the beginning of the reaction, the experiment was repeated with the same amounts of reagents. 2 minutes after the precipitate began to form the reaction mixture was cooled in ice. The weight of the precipitate was 2.4 g, m. p. 138° (decomp.). The compound decolorized bromine water and reduced permanganate.

Found %: N 4.86, 4.95. $C_{17}H_{17}O_4N$. Calculated %: N 4.68.

The yield of the acid salt of benzylamine and benzalmalonic acid was 77%.

Treatment of 1 g of the salt with hydrochloric acid yielded 0.53 g of a crystalline substance which gave no melting point depression with benzalmalonic acid after recrystallization from water.

1 g of benzylammonium acid benzylmalonate was heated 4 hours in anhydrous alcohol, when the precipitate dissolved completely. 0.36 g (72.7%) of cinnamic acid was isolated from the alcohol solution.

b) A mixture of 4 g of benzalbenzylamine, 2.2 g of malonic acid, and 20 ml of anhydrous benzene was heated 8 hours on the water bath. At the end of the reaction anhydrous ether was added for complete precipitation of the amino acid. The precipitate was recrystallized from 70% ethyl alcohol. Yield 2.4 g (45.9%). M. p. 177°.

0.95 g (31.6%) of cinnamic acid was isolated from the ether-benzene mother liquor.

Synthesis of β-N-ethylamino-β-phenylpropionic acid. a) 2 g of benzalethylamine, 1.5 g of malonic acid, and 10 ml of anhydrous alcohol was heated on the water bath. At 45° formation of a precipitate and evolution of gas bubbles commenced. The heating at the boil was continued 4 hours, and the precipitate did not dissolve completely. The weight of the precipitate was 2.55 g, m. p. 145° (decomp.). The substance was easily soluble in water, decolorized bromine water, and reduced permanganate. Ethylamine was evolved by the action of alkalies.

Treatment of 0.8 g of the substance with hydrochloric acid yielded 0.55 g of benzalmalonic acid, m. p. 192° (from water).

The yield of the acid salt of benzylamine and benzalmalonic acid was 72.9%.

Found %: N 5.99, 6.26. $C_{12}H_{15}O_4N$. Calculated %: N 5.91.

1 g of ethylammonium acid benzalmalonate and 8 ml of anhydrous alcohol were boiled 12 hours, when the precipitate dissolved. Evaporation of the alcohol solution and hydrochloric acid treatment yielded 0.45 g (72%) of cinnamic acid.

The alcoholic mother liquor which remained after isolation of ethylammonium acid benzalmalonate gradually yielded β-N-ethylamino-β-phenylpropionic acid by the action of anhydrous ether. After recrystallization from alcohol the m. p. was 167-168°. Yield 0.15 g (5.15%). The substance is soluble in water, and with difficulty in benzene.

Found %: N 7.34, 7.34. $C_{11}H_{15}O_2N$. Calculated %: N 7.25.

Evaporation of the ether-alcohol mother liquor and hydrochloric acid treatment of the residue yielded 0.25 g (11.2%) of cinnamic acid.

b) 4 g of benzalethylamine, 3 g of malonic acid, and 20 ml of anhydrous benzene were boiled on the water bath. A white crystalline precipitate gradually formed. After 4 hours of heating the reaction mixture was gradually cooled and the precipitate was separated from the solution. Yield 5.35 g, m. p. 130° (decomp.). The precipitate was a mixture of ethylammonium acid benzalmalonate and β-N-ethylamino-β-phenylpropionic acid. After twofold treatment with hot anhydrous alcohol the melting point of the undissolved ethylammonium acid benzalmalonate rose to 143-144° (decomp.). Weight 4.4 g (62%). 0.6 g (10.3%) of β-N-ethylamino-β-phenylpropionic acid was obtained from the alcohol on cooling.

The benzene mother liquor yielded 0.25 g (5.6%) of cinnamic acid.

Synthesis of β-(N-nitrose-N-ethylamino)-β-phenylpripionic acid. To a solution of 0.2 g of β-N-ethylamino-β-phenylpropionic acid in 2 ml of 5% hydrochloric acid a solution of 0.15 g of sodium nitrite in 3 ml of water was gradually added. At 30-35° drops of oil separated, which crystallized on standing into long thin needles with m. p. 69-70°.

Found %: N 12.64, 12.68. $C_{11}H_{14}O_3N_2$. Calculated %: N 12.61.

Synthesis of β-N-propylamino-β-phenylpropionic acid. a) 5.8 g of benzalpropylamine, 4 g of malonic acid, and 32 ml of anhydrous benzene was boiled 7 hours. A precipitate of β-N-propylamino-β-phenylpropionic acid gradually formed. The precipitate was filtered off, washed with ether, and recrystallized from 50% alcohol. The yield was 3.3 g (40.5%) of platelets with m. p. 176-177°. The amino acid is easily soluble in water, much less easily in ethyl alcohol, and with difficulty in benzene.

Found %: N 6.88, 6.66. $C_{12}H_{17}O_2N$. Calculated %: N 6.76.

1.5 g (26%) of cinnamic acid was isolated from the benzene mother liquor after evaporation and treatment of the residue with hydrochloric acid.

b) A mixture of 2.8 g of benzalpropylamine, 2 g of malonic acid, and 16 ml of anhydrous alcohol was boiled 4 hours on the water bath; no precipitate was formed. At the end of the reaction the alcohol was partly driven off and the amino acid precipitated by anhydrous ether. After recrystallization from 50% alcohol, 0.5 g (12.56%) of β-N-propylamino-β-phenylpropionic acid, m. p. 177°, was obtained. The ether-alcohol mother liquor, after evaporation and treatment of the residue with hydrochloric acid, yielded 1.65 g (57.0%) of cinnamic acid.

Synthesis of β-(N-nitrose-N-propylamino)-β-phenylpropionic acid. To a solution of 0.4 g of β-N-propylamino-β-phenylpropionic acid in 5 ml of 5% hydrochloric acid a solution of 0.2 g of sodium nitrite in 2 ml of water was added. Gentle heating resulted in the formation of drops of an oil which crystallized on standing in the form of slightly yellowish needles. After recrystallization from water the compound was precipitated in the form of needles clustered into nodules.

Found %: N 12.22, 12.15. $C_{12}H_{16}O_3N_2$. Calculated %: N 11.87.

SUMMARY

1. It is established that the intermediate product formed in the reaction for the preparation of β-N-methylamino-β-phenylpropionic acid, described by Evans and Johnson and identified by them as β-phenyl-β-methylamino-α, α-ethanedicarboxylic acid, is the acid salt of benzalamlonic acid and methylamine.

2. The following β-amino acids were synthesized: β-N-ethylamino-β-phenylpropionic and its nitroso derivative, β-N-propylamino-β-phenylpropionic and its nitroso derivative, and β-N-benzylamino--β-phenylpropionic.

3. The intermediate reaction products in the preparation of the β-amino acids, ethylammonium acid benzylmalonate and benzylammonium acid benzalmalonate, were isolated and studied.

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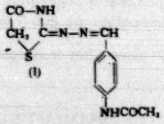
SYNTHESIS OF THIAZOLIDONE DERIVATIVES OF BIOLOGICAL INTEREST

II. DERIVATIVES OF THIAZOLIDINEDIONE-2, 4-HYDRAZONE-2, OBTAINED FROM THIBONE

E. V. Vladzimirskaya and N. M. Turkevich

In the previous communication it was shown that thiosemicarbazones can be easily converted into derivatives of thiazolidone-4 by condensation with chloroacetic acid in the presence of glacial acetic acid. This was used for an attempt to prepare these derivatives from thibone, which is of definite interest, as the introduction of thiazolidine rings into the molecule is usually accompanied by a decrease in the toxicity of the product [1, 2].

When thibone and chloroacetic acid are heated in acetic acid solution, a precipitate of thiazolidenedione-p-acetaminobenzylidenehydrazone (I) is formed. This substance has clearly defined acid properties and dissolves on gentle heating not only in solutions of NaOH and soda, but in sodium bicarbonate. The substance dissolves in ammonia even in the cold, in contrast to thibone, which also has certain acid properties.



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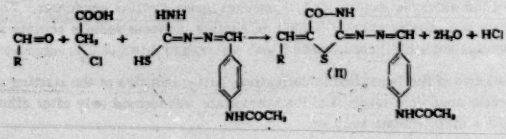
The acid properties of thiazolidinedione-p-acetaminobenzylidenehydrazone should be attributed to the presence of the CONH amide group in the molecule. The substance is insoluble in typical organic solvents (ether, benzene, chloroform).

In view of the poor solubility of thiazolidinedione-p-acetaminobenzylidenehydrazone in glacial acetic acid, its 5-arylidene derivatives are better prepared by a method different from that used for the other thiazolidone derivatives [3], that is, not by condensation with aromatic aldehydes in acetic acid, but directly from thibone:

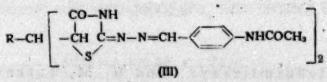


(II)

When thibone, chloroacetic acid, and various aldehydes (p-methoxybenzoic, o-chlorobenzoic, cinnamic) are boiled in glacial acetic acid, clear solutions are formed, from which 5-arylidene derivatives are obtained after the solutions are cooled or diluted with aqueous sodium acetate solution. When p-acetaminobenzoic aldehyde is used, the 5-p-acetaminobenzylidene derivative, sparingly soluble in boiling acetic acid, is precipitated even from the boiling solution.

The introduction of arylidene groups into the thiazolidinedione-p-acetaminobenzylidenehydrazone molecule increases the solubility of the products in typical organic solvents, but the solubility still remains low. Of the compounds obtained, the 5-p-acetaminobenzylidene and 5-p-methoxybenzylidene derivatives have clearly defined acid properties.

When thibone was heated with chloroacetic acid and benzoic and salicylic aldehydes in glacial acetic acid, the products were not the usual 5-arylidene derivatives (II), but substances (III) in which the arylidene group links two thiazolidinedione-p-acetaminobenzylidenehydrazone residues. These compounds dissolve in aqueous ammonia even in the cold.



(III)

Thiazolidinedione-p-acetaminobenzylidenehydrazone (I), like all its 5-arylidene derivatives synthesized, gives a characteristic dark red color when heated with p-dimethylaminobenzaldehyde and 2 drops of concentrated hydrochloric acid. This reacton depends on the presence of a p-acetaminobenzylidene group, as the red color was observed not only with thibone, but with p-acetaminobenzaldehyde. Of the p-aminobenzoic acid derivatives, novocaine and thiocaine give this reaction, but with a much weaker color. Anesthesine and PASK do not give a red color in the conditions stated.

The action of sodium nitrite on a solution of thibone in 50% sulfuric solution results in the formation of an intense orange-red color [4]. The thiazolidone derivatives obtained by us from thibone do not give this reaction.

When (I), and also its benzylidene-bis, cinnamylidene, and salicylidene-bis derivatives, are boiled 1 minute with 10% NaOH solution, partial splitting of the thiazolidine ring already takes place, as subsequent addition of sodium nitroprusside produces a dark red or violet (turning to red) color. The anisylidene, o-chlorobenzylidene, and p-acetaminobenzylidene derivatives are much more stable and do not give this reaction.

The formation of lead sulfide only took place after prolonged boiling of the substances synthesized with alkaline sodium plumbite solution.

EXPERIMENTAL

Thiazolidinedione-2, 4-p-acetaminobenzylidenehydrazone-2 (I). 2.5 g of thibone, 1.17 g of chloroacetic acid, and 22 ml of glacial acetic acid was boiled 2 hours under a reflux condenser. The product was diluted with aqueous sodium acetate solution (5 g). The precipitate was filtered off, washed with water, and dried. The yield was 2.7 g (92.4%) of a substance with a lemon-yellow color, which decomposed at 294° [5] (from acetic acid), easily soluble in ammonia and concentrated hydrochloric acid, and on heating in alcohol, glycerol, and dioxane, and also in solutions of soda, sodium bicarbonate, and 10% NaOH.

5-Arylidene derivatives of thiazolidinedione-2, 4-p-acetaminobenzylidenehydrazone-2. 5.0 g of the thiosemicarbazone of p-acetaminobenzaldehyde, 2.35 g of chloroacetic acid, 20 ml of glacial acetic acid, and 25-27 millimoles of the aldehyde were boiled 30 minutes under a reflux condenser. To the reaction mixture, in which a precipitate was usually already formed on cooling, aqueous sodium acetate solution (10 g) was added, and the resultant precipitate was filtered, washed with water, and dried.

For the preparation of the benzylidene derivative, half-quantities of the starting substances dissolved in 20 ml of glacial acetic acid were taken, and the precipitate was formed only after dilution of the reaction product with aqueous sodium acetate solution.

Name of Compound	Formula	Yield (%)	Melting Point	Analysis for N (in %)	
				Found	Calculated
Thiazolidinedione-2, 4-p-acetaminobenzylidenehydrazone-2	$C_{11}H_{10}O_2N_4S$ (I)	92.4	about 294° (decomp.)	20.34	20.28
5-Benzylidene-bis-thiazolidinedione-2, 4-p-acetaminobenzylidenehydrazone-2	$C_{21}H_{20}O_2N_6S_2$ (III, R = C_6H_5)	80	263°	17.44*	17.49
5-Anisylidenethiazolidinedione-2, 4-p-acetaminobenzylidenehydrazone-2	$C_{20}H_{18}O_3N_4S$ (II, R = p-$CH_3OC_6H_4$)	81	> 230° (decomp.)	14.32	14.21
5-o-Chlorobenzylidenethiazolidinedione-2, 4-p-acetaminobenzylidenehydrazone-2	$C_{19}H_{15}O_2N_4ClS$ (II, R = o-ClC_6H_4)	89	> 230° (decomp.)	14.23	14.05
5-Cinnamylidenethiazolidinedione-2, 4-p-acetaminobenzylidenehydrazone-2	$C_{21}H_{18}O_2N_4S$ (II, R = $C_6H_5CH=CH$)	85	about 190° (decomp.)	14.30	14.35
5-Salicylidene-bis-(thiazolidinedione-2, 4-p-acetaminobenzylidenehydrazone-2)	$C_{21}H_{20}O_3N_6S_2$ (III, R = o-HOC_6H_4)	86	> 230° (decomp.)	16.97	17.07
5-Acetaminobenzylidenethiazolidinedione-2, 4-p-acetaminobenzylidenehydrazone-2	$C_{21}H_{19}O_3N_5S$ (II, R = p-$CH_3CONHC_6H_4$)	82	> 275°	16.42	16.62

* Found %: C 58.49; H 4.65. Calculated %: C 58.11; H 4.40.

The dried condensation products were crystallized from glacial acetic acid and analyzed. The results are shown in the Table. The purification of 5-p-acetaminobenzylidenethiazolidinedione-2, 4-p-acetaminobenzylidenehydrazone-2 was effected not by crystallization, which was difficult, but by reprecipitation by ligroine from nitrobenzene solution.

The benzylidene derivative is an orange-yellow substance, the p-acetaminobenzylidene derivative is yellow, and the other condensation products are dark yellow.

SUMMARY

1. The synthesis of seven different derivatives of thiazolidinedione-2, 4-hydrazone-2, with thibone as the starting material, is described. Most of the substances obtained have acid properties.

2. 5-Arylidene derivatives of thiazolidinedione-2, 4-hydrazone-2 may be prepared by the direct heating of aromatic aldehydes, thiosemicarbazones, and chloroacetic acid in glacial acetic acid.

3. The characteristic reactions of thiazolidinedione-2, 4-hydrazone-2 derivatives are described.

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NITRATION OF ar-TETRAHYDRONAPHTHALENE-2-CARBOXYLIC ACID AND TRANSFORMATIONS OF 1-NITRO- AND 4-NITRO-5,6,7,8-TETRAHYDRONAPHTHALENE-2-CARBOXYLIC ACIDS

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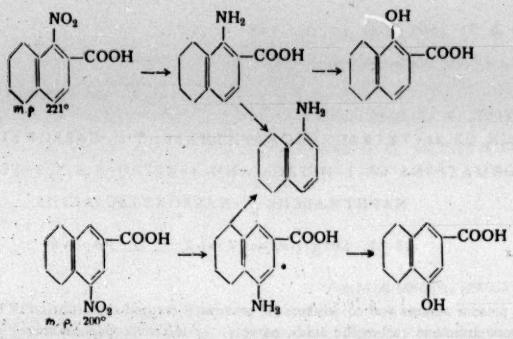
One of the present authors and co-workers [1] previously studied the nitration of three of the possible and known tetrahydronaphthalene carboxylic acids, namely: ar-tetrahydronaphthalene-1-carboxylic and ac-tetrahydronaphthalene-1- and 2-carboxylic. In the present study the nitration of ar-tetrahydronaphthalene--2-carboxylic acid was performed for the first time, different methods for carrying out the reaction being used. Positive results were obtained by nitration with excess of nitric acid (d 1.5) and also by nitration with a mixture of potassium nitrate and sulfuric acid. In both instances two nitro acids were isolated: a larger quantity (27.6 and 30%) of 1-nitro-5,6,7,8-tetrahydronaphthalene-2-carboxylic (m.p. 221°), and a smaller quantity (5.4 and 3.4%) of 4-nitro-5,6,7,8-tetrahydronaphthalene-2-carboxylic (m.p. 200°). The methods for the separation of the isomeric acids differed according to the method of preparation: when the nitration was effected by a mixture of potassium nitrate and sulfuric acid, the separation of the nitro acids formed was fairly easy, and could be achieved by means of recrystallization; with nitration by nitric acid (d 1.5), despite the fact that the greater part of the ar-1-nitrotetrahydronaphthalene-2-carboxylic acid was already precipitated from the nitric acid medium during the nitration, separation of the mixture of nitro acids isolated from the mother liquors was long and laborious, as it required additional transformations (esterification, saponification of the esters, etc.).

For determination of the structure of the nitro acids obtained, they were subjected to transformations which might lead to tetrahydronaphthalene compounds of already known structure. The nitro groups in both acids were reduced catalytically to give different amino acids, which were then decarboxylated; ar-α-tetrahydronaphthylamine was formed, identified as its acetyl derivative. The formation of the same tetrahydronaphthylamine from both amino acids showed that in these, and therefore in the original nitro acids, the nitro groups occupy the α-position in the tetrahydronaphthalene ring, and therefore the acids obtained were 1-nitro- and 1-amino- and 4-nitro- and 4-amino-5,6,7,8-tetrahydronaphthalene-2-carboxylic. In order to determine which of these acids correspond to the (1,2) or (4,2) positions of the substituents, the amino acids were converted into the corresponding hydroxy acids by diazotization and decomposition of the diazo compounds. Comparison of these hydroxy acids with the known 1-hydroxy-5,6,7,8-tetrahydronaphthalene-2-carboxylic acid, which we synthesized from ar-α-tetralol by a method described in the literature [2], showed that one of them is identical with 1-hydroxy-5,6,7,8-tetrahydronaphthalene-2-carboxylic acid, and this determined the structure of the other hydroxy acid, which could only be 4-hydroxy-5,6,7,8-tetrahydronaphthalene-2-carboxylic, as the α-position of the hydroxyl group in it was clear from the above. From these data it was possible to deduce the structure of the original nitro and amino acids (see Scheme on following page).

We also prepared various derivatives of 1(4)-nitro-and 1(4)-amino-5,6,7,8-tetrahydronaphthalene-2--carboxylic acids.

EXPERIMENTAL

Nitration of ar-tetrahydronaphthalene-2-carboxylic acid by nitric acid (d 1.5). 1-Nitro-5,6,7,8, tetrahydronaphthalene-2-carboxylic acid. 35.2 g (0.2 mole) of ar-tetrahydronaphthalene-2-carboxylic acid (m.p. 151-152°) was added during 45 minutes with vigorous stirring and external cooling at a temperature not above 0° to 43 ml of nitric acid (d 1.50) (1 mole), the stirring was continued at the same temperature a further 30 minutes, the copious precipitate was filtered off, washed with water, and recrystallized twice from dichloroethane, after which the substance melted at 221°. The yield in ten such experiments was 137.6 g (31.1%).



1-Nitro-5,6,7,8-tetrahydronaphthalene-2-carboxylic acid crystallizes from dichloroethane in the form of colorless needles, is soluble in acetone, ether, ethyl acetate, and methyl and ethyl alcohol, dissolves with difficulty in boiling benzene, and is insoluble in ligroine and water.

Found %: C 59.84, 59.62; H 4.80, 4.72; N 6.11, 6.06. $C_{11}H_{11}O_4N$. Calculated %: C 59.72; H 5.01; N 6.33.

4-Nitro-5,6,7,8-tetrahydronaphthalene-2-carboxylic acid. Dichloroethane was driven off from the mother liquors obtained after recrystallization of 1-nitro-5,6,7,8-tetrahydronaphthalene-2-carboxylic acid from dichloroethane in 10 nitration experiments, after which 185 g of a substance with m.p. 138-150°* remained. This substance was esterified by boiling it 10 hours with three times the amount of anhydrous ethyl alcohol saturated with hydrogen chloride. After the usual treatment the ester mixture was stirred with 250 ml of ethyl alcohol, the undissolved crystalline substance was filtered off and recrystallized from ethyl alcohol, when the ethyl ester of 1-nitro-5,6,7,8-tetrahydronaphthalene-2-carboxylic acid, m.p. 107-108°, is first precipitated. Yield 26.5 g (5.3%). The alcohol filtrate after separation of the crystalline precipitate was combined with the alcohol mother liquor obtained after recrystallization of this precipitate, the alcohol was driven off, and the residue distilled under vacuum. Most of the substance distilled at 180-186° at 3 mm. When the distillate was stirred with a small amount of methyl alcohol, it crystallized; the crystalline substance was pressed out, dried in the air, and saponified by means of 8-hour boiling with the equivalent amount of 0.5 N caustic potash solution. After the usual treatment the mixture of salts was dissolved in water and acidified with dilute hydrochloric acid, 2/3 of a mole for each mole of caustic potash taken for the saponification. The precipitate formed was filtered off, washed with water, dried, and twice recrystallized from methyl alcohol. The yield was 20 g of 4-nitro-5,6,7,8-tetrahydronaphthalene-2-carboxylic acid, m.p. 200°. The alcohol mother liquors were combined and concentrated; the precipitate formed was twice recrystallized from methyl alcohol, when 4 more grams of the same acid, m.p. 198°, was obtained. Yield 24 g (5.4%).

4-Nitro-5,6,7,8-tetrahydronaphthalene-2-carboxylic acid is a yellowish crystalline substance, m.p. 200°, soluble in the cold in ether, acetone, ethyl acetate, and ethyl alcohol; on warming, in methyl alcohol, dichloroethane, and benzene; and insoluble in ligroine and water.

Found %: C 59.90, 59.72; H 4.90, 5.03; N 6.08, 6.12. $C_{11}H_{11}O_4N$. Calculated %: C 59.72; H 5.01; N 6.33.

Nitration by a solution of potassium nitrate in sulfuric acid. 15 g of 5,6,7,8-tetrahydronaphthalene-2-carboxylic acid was dissolved in 65 ml of concentrated sulfuric acid, and a solution of 8.7 g of potassium

* Experiments for the isolation of individual compounds from the mixture with m.p. 138-150° by recrystallization did not give positive results.

nitrate in 20 ml of concentrated sulfuric acid was then added during 1 hour with stirring and external cooling, the temperature being maintained between 0 and +5°; at the end of the addition the stirring was continued at the same temperature 30 more minutes, when the reaction mixture was poured into cold water; the precipitate formed was filtered off, washed with water, and recrystallized from dichloroethane. The yield was 5 g of 1-nitro-5,6,7,8-tetrahydronaphthalene-2-carboxylic acid, m.p. 221°.

Dichloroethane was distilled off from the mother liquor after the second recrystallization to a 25 ml volume, and the substance which separated out was filtered off and recrystallized from dichloroethane. A further 0.2 g (27.6%) of the same acid, m.p. 220°, was obtained. From the mother liquor after the first recrystallization dichloroethane was driven off, the substance which partly crystallized on cooling was filtered off, and recrystallized from 5 ml of methyl alcohol. 0.7 g (3.6%) of a substance with m.p. 197-200° was obtained. A sample mixed with 4-nitro-5,6,7,8-tetrahydronaphthalene-2-carboxylic acid gave no melting point depression.

1-Amino-5,6,7,8-tetrahydronaphthalene-2-carboxylic acid. 30 g of 1-nitro-5,6,7,8-tetrahydronaphthalene-2-carboxylic acid (m.p. 221°) was dissolved in 450 ml of ethyl alcohol, 30 g of Raney nickel catalyst was added, and the mixture shaken in hydrogen under atmospheric pressure and gentle heating during 6 hours. After absorption of the calculated amount of hydrogen the catalyst was filtered off and the alcohol distilled off under vacuum. Yield 20.3 g (78%). After recrystallization from dichloroethane, 1-amino-5,6,7,8-tetrahydronaphthalene-2-carboxylic acid melts at 185° (decomp.), and is a colorless crystalline substance. The melting point varies according to the time of heating and the rate of temperature rise. The value m.p. 185° was obtained when the capillary was introduced into the apparatus previously heated to 160°, with the temperature rising 2° per minute. The acid is easily soluble in acetone, dissolves on heating in ethyl and methyl alcohols, benzene, and ethyl acetate, dissolves with difficulty in boiling ligroine and is insoluble in water;

Found %: C 69.06, 68.95; H 6.86, 6.79; N 7.21, 7.16. $C_{11}H_{13}O_2N$.
Calculated %: C 69.09; H 6.85; N 7.32.

4-Amino-5,6,7,8-tetrahydronaphthalene-2-carboxylic acid. 15 g of 4-nitro-5,6,7,8-tetrahydronaphthalene-2-carboxylic acid (m.p. 200°) was dissolved in 450 ml of ethyl alcohol, 15 g of Raney nickel catalyst was added, and the mixture shaken in hydrogen under atmospheric pressure and gentle heating during 2 hours. After absorption of the calculated amount of hydrogen and the usual treatment, 12.2 g (94%) of substance was obtained. After recrystallization from ethyl alcohol, 4-amino-5,6,7,8-tetrahydronaphthalene-2-carboxylic acid melts at 192-193° and consists of an almost colorless crystalline substance; it dissolves in acetone, methyl and ethyl alcohol, and ethyl acetate on heating, with difficulty in ether and in dichloroethane, and is insoluble in ligroine and water.

Found %: C 69.13, 68.90; H 6.76, 7.03; N 7.17. $C_{11}H_{13}O_2N$.
Calculated %: C 69.09; H 6.85; N 7.32.

Decarboxylation of 1-amino- and 4-amino-5,6,7,8-tetrahydronaphthalene-2-carboxylic acid. A mixture of 0.5 g of 1-amino-5,6,7,8-tetrahydronaphthalene-2-carboxylic acid and 1 g of barium hydroxide was subjected to dry distillation under vacuum (pressure 30 mm), the distillate was extracted with ether, the ether solution washed with caustic potash solution and dried with caustic potash, and excess of acetic anhydride was added. The crystalline substance formed was filtered off and twice recrystallized from ethyl acetate. The acetylaminotetrahydronaphthalene formed had m.p. 158°. A sample mixed with 1-acetylamino-5,6,7,8-tetrahydronaphthalene gave no melting point depression.

4-Amino-5,6,7,8-tetrahydronaphthalene-2-carboxylic acid wad decarboxylated in a similar way; the result was an amine the acetyl derivative of which was also identical with 1-acetylamino-5,6,7,8-tetrahydronaphthalene.

1-Hydroxy-5,6,7,8-tetrahydronaphthalene-2-carboxylic acid. To 12 g of 1-amino-5,6,7,8-tetrahydronaphthalene-2-carboxylic acid (m.p. 185° with decomp.), 19.2 ml of hydrochloric acid (d 1.184) was added and the mixture stirred 30 minutes, after which 60 ml of water was added, the mixture cooled, and a solution of 4.32 g of sodium nitrite in 15 ml of water was gradually added with vigorous stirring at a temperature not above 0°. The contents of the flask were then poured into 600 ml of ice-cold water, when

the diazo compound dissolved; the solution was quickly filtered and the filtrate heated on the water bath at 40-50°. On cooling, the hydroxy acid separated out in a yield of 10.9 g (90%). After recrystallization from dichloroethane the m.p. was 166.5-167.5°. A sample mixed with 1-hydroxy-5,6,7,8-tetrahydronaphthalene-2-carboxylic acid prepared by the carboxylation of ar-α-tetralol gave no melting point depression.

1-Hydroxy-5,6,7,8-tetrahydronaphthalene-2-carboxylic acid is a colorless crystalline substance soluble in ethyl alcohol and ethyl acetate in the cold, and in benzene on heating.

Found %: C 68.51, 68.68; H 6.26, 6.34. $C_{11}H_{12}O_3$. Calculated %: C 68.71; H 6.29.

4-Hydroxy-5,6,7,8-tetrahydronaphthalene-2-carboxylic acid. 37 ml of hydrochloric acid was added to 20 g of 4-amino-5,6,7,8-tetrahydronaphthalene-2-carboxylic acid (m.p. 192-193°) and the mixture was stirred 30 minutes, 100 ml of water was then added and the acid diazotized by a mixture of 7.2 g of sodium nitrite in 25 ml of water at a temperature not above 0°; the substance dissolved in the process. After 15 minutes the contents of the flask were poured into 1 liter of ice-cold water, the solution was quickly filtered and the filtrate was heated at 40° on the water bath. The precipitated hydroxy acid (yield 17.4 g, 86.5%) was recrystallized from dichloroethane.

4-Hydroxy-5,6,7,8-tetrahydronaphthalene-2-carboxylic acid is a slightly yellowish crystalline substance, m.p. 192-194°, soluble in acetone, ether, ethyl acetate, and methyl and ethyl alcohols.

Found %: C 68.52; H 6.21. $C_{11}H_{12}O_3$. Calculated %: C 68.71; H 6.29.

Derivatives of 1-nitro-5,6,7,8-tetrahydronaphthalene-2-carboxylic acid. Ethyl ester. 10 g of 1-nitro-5,6,7,8-tetrahydronaphthalene-2-carboxylic acid was boiled 7 hours with 100 ml of anhydrous ethyl alcohol saturated with hydrogen chloride. After the usual treatment 9.6 g (85%) of substance was obtained. After recrystallization from ethyl alcohol, the ethyl ester of 1-nitro-5,6,7,8-tetrahydronaphthalene-2-carboxylic acid is a colorless crystalline substance, m.p. 109°; b.p. 164° at 2 mm, soluble in ether, acetone, benzene, ethyl acetate, dichloroethane, boiling ethyl alcohol, and ligroine.

Found %: N 5.51, 5.56. $C_{13}H_{15}O_4N$. Calculated %: N 5.62.

Methyl ester. This was prepared by an analogous method. Yield 94%. After recrystallization from methyl alcohol, the methyl ester of 1-nitro-5,6,7,8-tetrahydronaphthalene-2-carboxylic acid consists of colorless needles, m.p. 149.5-150°, soluble in benzene and acetone, and on heating in ethyl acetate.

Found %: N 5.92. $C_{12}H_{13}O_4N$. Calculated %: N 5.95.

Acid chloride. 20 g of the acid was heated with 50 g of thionyl chloride 3 hours at bath temperature 65°. After removal of thionyl chloride under vacuum, the crystalline residue was washed several times with anhydrous ether. Yield 20 g (92%). After recrystallization from anhydrous ether, the acid chloride of 1-nitro-5,6,7,8-tetrahydronaphthalene-2-carboxylic acid melts at 97-98°; it is a colorless crystalline substance soluble in ethyl acetate, anhydrous benzene, and chloroform.

Found %: Cl 14.91, 14.91. $C_{11}H_{10}O_3NCl$. Calculated %: Cl 14.79.

Amide. 0.5 g of the acid chloride of 1-nitro-5,6,7,8-tetrahydronaphthalene-2-carboxylic acid was stirred with 10 ml of 19% ammonia solution. Yield 0.45 g (98%). After recrystallization from ethyl alcohol, 1-nitro-5,6,7,8-tetrahydronaphthalene-2-carboxylic acid amide consists of almost colorless shiny platelets with m.p. 218-219.5°, soluble in ethyl alcohol and ethyl acetate on warming, insoluble in ether.

Found %: N 12.57. $C_{11}H_{12}O_3N_2$. Calculated %: N 12.72.

Hydrazide. 15 g of the ethyl ester of 1-nitro-5,6,7,8-tetrahydrohaphthalene-2-carboxylic acid was dissolved with warming in 30 ml of anhydrous ethyl alcohol, 9 g of hydrazine hydrate was added, and the mixture heated 8 hours on the boiling water bath. The yield of the crude substance was 10.7 g (75%). After recrystallization from ethyl alcohol the hydrazide of 1-nitro-5,6,7,8-tetrahydronaphthalene-2-carboxylic acid is a colorless crystalline substance with m.p. 163°, soluble in dichloroethane and methyl alcohol, insoluble in ether and water.

Found %: N 17.98. $C_{11}H_{13}O_3N_3$. Calculated %: N 17.86.

Derivatives of 4-nitro-5,6,7,8-tetrahydronaphthalene-2-carboxylic acid. Ethyl ester. This was prepared by the same method as the ethyl ester of 1-nitro-5,6,7,8-tetrahydronaphthalene-2-carboxylic acid. After the usual treatment it was distilled under vacuum, b.p. 188.5° at 6 mm. Yield 88%. After recrystallization from methyl alcohol the ethyl ester of 4-nitro-5,6,7,8-tetrahydronaphthalene-2-carboxylic acid consists of pale yellow needles with m.p. 52-52.5°, soluble in the usual organic solvents.

Found %: N 5.49. $C_{13}H_{15}O_4N$. Calculated %: N, 5.62.

Methyl ester. This was prepared similarly. Yield 90%. After recrystallization from ethyl alcohol the methyl ester of 4-nitro-5,6,7,8-tetrahydronaphthalene-2-carboxylic acid is a yellowish crystalline substance, easily soluble in dichloroethane, ligroine, benzene, methyl alcohol, and ethyl acetate.

Found %: N 6.09. $C_{12}H_{13}O_4N$. Calculated %: N 5.95.

Acid chloride. 12 g of the acid was heated with 30 g of thionyl chloride 1.5 hours at 65° bath temperature. Thionyl chloride was driven off under vacuum, and the residue was distilled under vacuum, b.p. 164-165° at 3 mm. Yield 10.6 g (82%). After a second vacuum distillation, b.p. 161-162° at 2 mm.

The acid chloride of 4-nitro-5,6,7,8-tetrahydronaphthalene-2-carboxylic acid is a yellowish substance, m.p. 50-51°, easily soluble in anhydrous ether, anhydrous benzene, and ligroine.

Found %: Cl 14.54. $C_{11}H_{10}O_3NCl$. Calculated %: Cl 14.79.

Hydrazide. 8 g of the ethyl ester of 4-nitro-5,6,7,8-tetrahydronaphthalene-2-carboxylic acid was dissolved with warming in 4 ml of anhydrous ethyl alcohol, 4.8 g of hydrazine hydrate was added, and the mixture heated 4 hours on the boiling water bath. 7.3 g (96%) of the substance was obtained.

The hydrazide of 4-nitro-5,6,7,8-tetrahydronaphthalene-2-carboxylic acid consists of large plates with a nacreous luster, m.p. 181.5-182°, soluble on heating in ethyl acetate and methyl alcohol, insoluble in ether and water.

Found %: N 17.73. $C_{11}H_{13}O_3N_3$. Calculated %: N 17.86.

Derivatives of 1-amino-5,6,7,8-tetrahydronaphthalene-2-carboxylic acid. Ethyl ester (hydrochloride). 8 g of the ethyl ester of 1-nitro-5,6,7,8-tetrahydronaphthalene-2-carboxylic acid was dissolved in 200 ml of ethyl acetate, placed in an autoclave, 8 g of Raney nickel catalyst was added, the autoclave filled with hydrogen to 20 atmospheres pressure, and hydrogenation effected at 40° during 1 hour. The catalyst was filtered off, the ethyl acetate was driven off under vacuum, and the residue — an oil — was dried under vacuum. 3 g of the resultant ethyl ester of 1-amino-5,6,7,8-tetrahydronaphthalene-2-carboxylic acid was dissolved in ether and an ether solution of hydrogen chloride was added with cooling and stirring. The precipitate was filtered off, washed several times with ether, and recrystallized from acetone.

The hydrochloride of the ethyl ester of 4-amino-5,6,7,8-tetrahydronaphthalene-2-carboxylic acid is a colorless crystalline substance, m.p. 165-167° (decomp.) soluble in cold dichloroethane and methyl and ethyl alcohols, soluble in benzene on heating, dissolved with difficulty on heating in ethyl acetate, insoluble in ether.

Found %: N 5.31. $C_{13}H_{17}O_2N \cdot HCl$. Calculated %: N 5.48.

Ethyl ester of 1-acetylamino-5,6,7,8-tetrahydronaphthalene-2-carboxylic acid. 1 g of the unpurified ethyl ester of 1-amino-5,6,7,8-tetrahydronaphthalene-2-carboxylic acid was thoroughly stirred with 4 ml of acetic anhydride. Excess acetic anhydride was driven off under vacuum. The substance which separated out was recrystallized from ligroine. The product consisted of colorless needles with m.p. 132.5-133.5°, soluble in acetone, ethyl acetate, benzene, dichloroethane, and methyl and ethyl alcohols.

Found %: N 5.18. $C_{15}H_{19}O_3N$. Calculated %: N 5.36.

Hydrazide. A mixture of 5 g of 1-nitro-5,6,7,8-tetrahydronaphthalene-2-carboxylic acid hydrazide, 500 ml of ethyl alcohol, and 5 g of Raney nickel catalyst was shaken in hydrogen 2.5 hours under atmospheric pressure with gentle heating. After the usual treatment and recrystallization from benzene, 1-amino-5,6,7,8-tetrahydronaphthalene-2-carboxylic acid hydrazide consists of a colorless crystalline substance, m.p. 147-148°, soluble in dichloroethane, and in ethyl and methyl alcohols, soluble in ethyl acetate on warming, and insoluble in water.

Found %: N 20.77. $C_{11}H_{15}ON_3$. Calculated %: N 20.47.

Derivatives of 4-amino-5,6,7,8-tetrahydronaphthalene-2-carboxylic acid. Ethyl ester. 5 g of the ethyl ester of 4-nitro-5,6,7,8-tetrahydronaphthalene-2-carboxylic acid, 175 ml of ethyl alcohol, and 5 g of Raney nickel catalyst were shaken 3 hours in hydrogen under atmospheric pressure. 4.2 g (95%) of a substance was obtained and recrystallized from ligroine. The ethyl ester of 4-amino-5,6,7,8-tetrahydronaphthalene-2-carboxylic acid melts at 65°, and is soluble in acetone, dichloroethane, ethyl acetate, benzene, and ethyl and methyl alcohols.

Found %: N 6.45. $C_{13}H_{17}O_2N$. Calculated %: N 6.39.

Hydrazide. 4.5 g of 4-nitro-5,6,7,8-tetrahydronaphthalene-2-carboxylic acid hydrazide, 450 ml of ethyl alcohol, and 4.5 g of Raney nickel catalyst was shaken 4 hours in hydrogen at atmospheric pressure with gentle heating. The substance obtained after the usual treatment was recrystallized from benzene-ethyl alcohol mixture (10 : 1).

4-Amino-5,6,7,8-tetrahydronaphthalene-2-carboxylic acid hydrazide is an almost colorless crystalline substance, m.p. 138.5-139.5°, easily soluble in methyl and ethyl alcohols, soluble on heating in dichloroethane, and insoluble in ether, ligroine, and benzene.

Found %: N 20.53. $C_{11}H_{15}ON_3$. Calculated %: N 20.47.

4-Acetylamino-5,6,7,8-tetrahydronaphthalene-2-carboxylic acid. 0.25 g of 4-amino-5,6,7,8-tetrahydronaphthalene-2-carboxylic acid was stirred with 4 ml of acetic anhydride, and the product recrystallized from ethyl alcohol.

4-Acetylamino-5,6,7,8-tetrahydronaphthalene-2-carboxylic acid is a white powder, soluble with difficulty in the usual organic solvents, m.p. 293° (decomp.) (with temperature rise of 5° per minute).

Found %: N 6.16. $C_{13}H_{15}O_3N$. Calculated %: N 6.00.

SUMMARY

1. In the nitration of 5,6,7,8-tetrahydronaphthalene-2-carboxylic acid, 1-nitro- and 4-nitro-5,6,7,8-tetrahydronaphthalene-2-carboxylic acids are formed.

2. The structure of the nitro acids formed was established by conversion into tetrahydronaphthalene compounds of known structure.

3. By catalytic hydrogenation of 1(4)-nitro-5,6,7,8-tetrahydronaphthalene-2-carboxylic acids the corresponding 1(4)-amino-5,6,7,8-tetrahydronaphthalene-2-carboxylic acids were prepared.

4. 1-Hydroxy- and 4-hydroxy-5,6,7,8-tetrahydronaphthalene-2-carboxylic acids were prepared from the corresponding aminotetrahydronaphthalene-2-carboxylic acids by diazotization and decomposition of the diazo compounds.

5. Derivatives of 1-nitro- and 4-nitro- and also of 1-amino- and 4-amino-5,6,7,8-tetrahydronaphthalene--2-carboxylic acids were prepared.

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* T.p. = C. B. translation pagination.

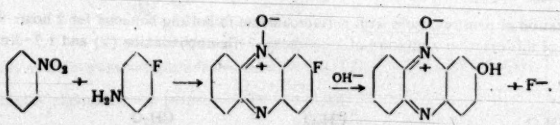
SYNTHESIS OF SOME FLUORINE DERIVATIVES OF PHENAZINE, AZOBENZENE, AND DIPHENYLAMINE

V. P. Chernetsky, L. M. Yagupolsky, and S. B. Serebryany

The fluorine derivatives of phenazine have been studied very little. Only two compounds of this class have been described: the N-oxide of 2,6-difluorophenazine [1], and the recently synthesized 2-fluorophenazine [2].

The present communication describes the synthesis of a number of phenazines, their N-oxides, and of some other fluorine-containing substances. These compounds were obtained mainly by the alkaline condensation of aromatic nitro compounds with aromatic amines. In addition, some fluorine derivatives of phenazine were synthesized by the reductive cyclization of the corresponding o-nitrodiphenylamines, and also by the condensation of o-benzoquinone with fluorine-containing o-phenylenediamines.

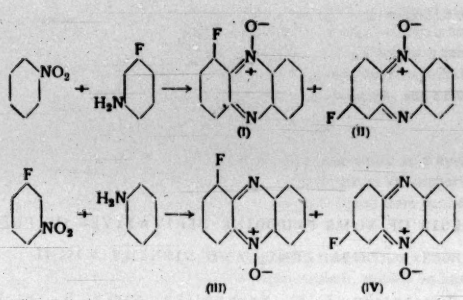
The preparation of 2-fluorophenazine, which had not been described at the start of this work, was effected by the alkaline condensation of nitrobenzene with p-fluoroaniline in boiling toluene during 9 hours. However, instead of the expected 2-fluorophenazine 9-oxide, 2-hydroxyphenazine 9-oxide was formed. The formation of the latter is apparently the result of a secondary exchange reaction of a fluorine atom for a hydroxyl group according to the following scheme:



As is known, fluorine atoms activated by electronegative groups in aromatic or heterocyclic systems in nucleophilic substitution reaction are exchanged more readily than other halogens [3]; therefore experiments on the condensation of nitrobenzene with p-fluoraniline in boiling benzene during 30 and 15 minutes were performed. In these mild condensation conditions it proved possible to isolate a small amount of 2-fluorophenazine. 2-Fluorophenazine was also obtained in a very low yield from 2-aminophenazine through the diazonium fluoborate, by Schimann's method. By the reductive cyclization of 2-nitro-4'-fluorodiphenylamine we succeeded in obtaining 2-fluorophenazine in 41% yield.

We attempted to synthesize 1-fluorophenazine by means of alkaline condensation of o-nitrofluorobenzene with aniline. However, even in mild conditions after brief heating in boiling benzene the reaction products were only o-nitrophenol and a small amount of o-nitrodiphenylamine.

1-Fluorophenazine was prepared by the condensation of m-fluoroaniline with nitrobenzene, and of m-nitrofluorobenzene with aniline. Closure of the phenazine ring by means of alkaline condensation in many instances leads to the formation of phenazine N-oxides. It has been shown that the oxygen atom in the N-oxide comes from the nitro group [4, 5], and therefore the above condensations should occur according to the following schemes:



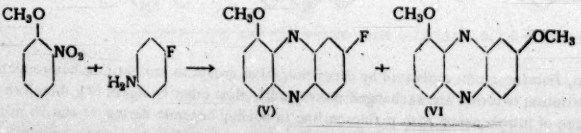
N-Oxides of type (I) are not usually formed during alkaline condensations, and the corresponding phenazines are formed instead [5-7]. The same was also found in the condensation of nitrobenzene with 3-fluoroaniline.

The N-oxides (II) and (IV) became converted into 2-hydroxyphenazine N-oxides. The oxide (III) was isolated. Apparently the fluorine atom in the 1 position, like the chlorine atom, has less tendency to nucleophilic substitution reactions than in the 2 position [8]. Halogen atoms are less mobile in phenazine than in phenazine N-oxide [8]; therefore it proved possible to isolate a small amount of 2-fluorophenazine from the condensation product of nitrobenzene with m-fluoroaniline.

Both reactions were continued 1 hour in boiling benzene. The first condensation gave 1-fluorophenazine in 5.6% yield and 2-fluorophenazine in 1.7% yield; the second condensation gave 1-fluorophenazine 10-oxide (III) in 2.8% yield, which was reduced to 1-fluorophenazine.

Thus, the condensation of nitrobenzene with m-fluoroaniline is the more convenient method for the synthesis of 1-fluorophenazine.

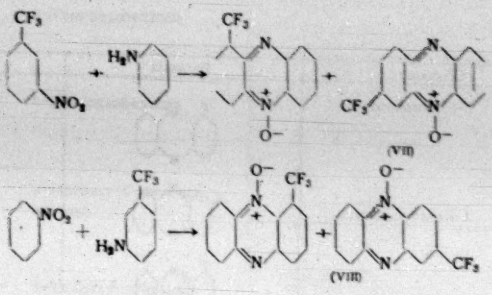
The condensation of o-nitroanisole with p-fluoroaniline in boiling benzene for 2 hours was also carried out. As the result of this reaction a mixture of 1-methoxy-7-fluorophenazine (V) and 1,7-dimethoxyphenazine (VI) was formed:



The formation of 1,7-dimethoxyphenazine takes place in the analogous instance of the condensation of o-nitroanisole with p-chloroaniline [9].

If the condensation of o-nitroanisole with p-fluoroaniline takes place during 4-6 hours in boiling toluene, the yield of 1-methoxy-7-fluorophenazine decreases and the amount of 1,7-dimethoxyphenazine increases. In this instance investigation of the aqueous alkaline solution obtained after the reaction mixture was poured into water showed that, in addition to the above-mentioned phenazine derivatives, 2-hydroxyphenazine and 1-methoxy-7-hydroxyphenazine are also formed. The structure of the latter was proved by conversion into 2-methoxyphenazine and 1,7-dimethoxyphenazine.

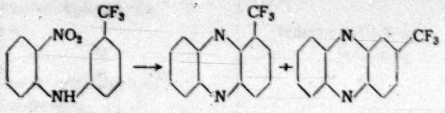
For the preparation of 1- and 2-trifluoromethylphenazines, two alkaline condensation reactions were investigated – that of m-nitrobenzo trifluoride with aniline, and of nitrobenzene with m-aminobenzo trifluoride. It was presumed that the reactions should proceed according to the following schemes:



In both instances only one N-oxide was isolated from the condensation products, and reduction of the N-oxides yielded the same 2-trifluoromethylphenazine. Its structure was established by a sample mixed with 2-trifluoromethylphenazine synthesized from o-quinone and 4-trifluoromethyl-o-phenylenediamine [10].

Thus, the condensation of m-nitrobenzo trifluoride with aniline resulted in the formation of 3-trifluoromethylphenazine 10-oxide (VII), and the condensation of nitrobenzene with m-aminobenzo trifluoride gave 2-trifluoromethylphenazine 10-oxide (VIII). Trifluoromethylphenazine and its N-oxides were not found in the products of these reactions.

As 2-nitro-3'-trifluoromethyldiphenylamine was available to us, we carried out its reductive cyclization with the aim of preparing 1- and 2-trifluoromethylphenazines according to the scheme:



However, only 2-trifluoromethylphenazine was isolated from the cyclization products.

1-Trifluoromethylphenazine was prepared from o-quinone and 3-trifluoromethyl-o-phenylenediamine [10].

Table 1 gives details of the fluorine derivatives of phenazine described in the present paper.

The products of the alkaline condensation carried out yielded, in addition to fluroine derivatives of phenazine, a number of o- and p-nitrodiphenylamines, azo and azoxy compounds containing fluorine, details of which are given in Table 2.

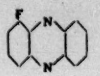
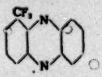
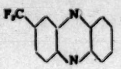
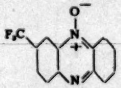
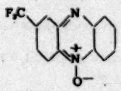
EXPERIMENTAL

The method for performing the alkaline condensation has been described previously [7, 9]. Any starting substances which did not react were distilled in steam. The residue was dissolved in benzene. The fluorophenazines were extracted from this solution by 20% hydrochloric acid, precipitated by aqueous ammonia, and then subjected to chromatographic separation on aluminum oxide from benzene solution.

The benzene solutions of the condensation products after treatment with hydrochloric acid contained azo and azoxy compounds and o- and p-nitrodiphenyl-amine derivatives. These were chromatographically separated on aluminum oxide. By these means the following individual compounds were isolated from the above complex mixtures.

1-Fluorophenazine. A mixture of 21.6 g of nitrobenzene, 11.1 g of m-fluoroaniline, 35 g of caustic potash, and 150 ml of benzene was boiled 1 hour. The condensation products yielded: 1.3 g (6.6%) of

TABLE 1

Serial No.	Compound	Formula	Melting point
1	1-Fluorophenazine		208-209°
2	2-Fluorophenazine		181-182
3	1-Fluorophenazine 10-oxide		203-204 (decomp. 220-225°)
4	1-Methoxy-7--fluorophenazine		150
5	1-Trifluoromethyl-phenazine		125-126
6	2-Trifluoromethyl-phenazine		177-178
7	2-Trifluoromethyl-phenazine 9-oxide		165-166
8	2-Trifluoromethyl-phenazine 10-oxide		153

1-fluorophenazine, pale yellow needles from alcohol, m.p. 208-209°, and 2-fluorophenazine, 0.33 g (1.7%), yellow needles from alcohol, m.p. 181-182° from aqueous alcohol. The latter substance did not give a melting point depression with 2-fluorophenazine prepared by the reductive cyclization of 2-nitro-4'-fluorodiphenylamine.

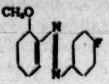
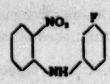
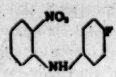
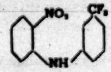
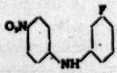
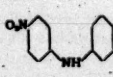
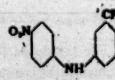
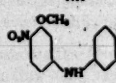
1-Fluorobenzine 10-oxide. A mixture of 14.1 g of m-nitrofluorobenzene, 9.3 g of aniline, and also including 23 g of caustic potash in 150 ml of benzene was used for the condensation. The mixture was boiled 1 hour. 1-Fluorophenazine 10-oxide was isolated from the reaction products, yield 0.62 g (2.8%). It forms long bright yellow needles from benzene, m.p. 203-204°, decomp. at 220-225°.

Found %: N 12.98, 12.87. $C_{12}H_7ON_2F$. Calculated %: N 13.08.

Reduction of this N-oxide yielded 1-fluorophenazine. This melted at the same temperature as the substance described above, and gave no melting point depression with it.

Found %: N 14.05, 14.03. $C_{12}H_7N_2F$. Calculated %: N 14.14.

TABLE 2

Serial No.	Compound	Formula	Melting point
9	3-Fluoroazobenzene		47-48°
10	4-Fluoroazobenzene		81-82 [11]
11	2-Methoxy-4'-fluoroazobenzene		68-70
12	3-Trifluoromethylazobenzene		37
13	3-Fluoroazoxybenzene		33-34
14	2-Nitro-3'-fluorodiphenylamine		74-75
15	2-Nitro-4'-fluorodiphenylamine		82-83
16	2-Nitro-3'-trifluoromethyldiphenylamine		66
17	4-Nitro-3'-fluorodiphenylamine		128-129
18	4-Nitro-4'-fluorodiphenylamine		191-192
19	4-Nitro-3'-trifluoromethyldiphenylamine		145
20	3-Methoxy-4-nitro-4'-fluorodiphenylamine		141-142

2-Fluorophenazine. a) A mixture of 24.6 g of nitrobenzene, 11.1 g of p-fluoroaniline, 36 g of caustic potash, and 150 ml of benzene was boiled 15 minutes. The reaction products yielded 0.15 g (0.78%) of 2-fluorophenazine. This forms pale yellow needles from aqueous alcohol, m.p. 181-182° (literature data [2]: m.p. 180.8-181.2°).

Found %: N 14.14, 14.04. $C_{12}H_7N_2F$. Calculated %: N 14.14.

When the condensation in boiling benzene lasted 30 minutes, traces of 2-fluorophenazine were formed.

In boiling toluene, with the use of a 5-fold excess of nitrobenzene, 2-hydroxyphenazine 9-oxide was formed in 35-40% yield. This forms small brown needles from glacial acetic acid, which decompose at 254-256° (described in the literature, decomposes at 258° [8]). Reduction of this compound by means of sodium hydrosulfite in alkaline solution yielded 2-hydroxyphenazine, the acetyl derivative of which melted at 155-156° and gave no melting point depression with known 2-acetoxyphenazine.

b) 0.8 g of 2-aminophenazine was treated with fluoboric acid solution prepared from 10 g of 40% hydrofluoric acid and 3.1 g of boric acid. 0.4 g of sodium nitrite dissolved in 2 ml of water was added to the mixture cooled to 0°, with vigorous stirring. At the end of the diazotization, the reaction mass was held 1 hour in a mixture of ice and salt. The brown precipitate of the diazonium salt was filtered off, and washed with water and then with acetone and ether, 1.1 g of the diazonium salt was obtained. This was dried in air and decomposed by heat. 2-Fluorophenazine was extracted from the reaction products by means of 20% hot hydrochloric acid. The acid extracts were combined and neutralized with ammonia. The contaminated 2-fluorophenazine was purified by filtration of the benzene solution through a small layer of aluminum oxide. After removal of the solvent the substance was crystallized from aqueous alcohol. The yields varied from 0.1 to 0.01 g, 181-182°.

b) A mixture of 1.4 g of 2-nitro-4'-fluorodiphenylamine and 0.8 g of active charcoal was heated in a long test tube to 250-300° and held 5 minutes at this temperature. The reaction products were extracted with boiling benzene. The benzene solution was chromatographically separated on aluminum oxide. The lower yellow zone yielded 0.4 g (41%) of 2-fluorophenazine with m.p. 179-181°, and the upper reddish brown zone yielded 0.25 g of unchanged 2-nitro-4'-fluorodiphenylamine.

No melting point depression was given by mixtures of 2-fluorophenazine samples obtained by all three methods.

1-Trifluoromethylphenazine. o-Benzoquinone was prepared by Willstatter's method [12], by the oxidation of a solution of 2.0 g of pyrocatechol in 150 ml of anhydrous ether with the aid of silver oxide prepared in this experiment from 20 g of silver nitrate. The resultant ether solution of the quinone was added to a solution of 2.0 g of 3-trifluoromethyl-o-phenylenediamine [10] in 50 ml of ether in the presence of 9 g anhydrous sodium sulfate. The mixture acquired a cherry color. After 2 days the sodium sulfate was filtered off, the solution was concentrated, and chromatographically separated on aluminum oxide. 0.125 g (4.5%) of 1-trifluoromethylphenazine was washed out with ligroine. The substance forms pale yellow needles from alcohol, m.p. 125-126°.

Found %: N 11.19. $C_{13}H_7N_2F_3$. Calculated %: N 11.29.

2-Trifluoromethylphenazine. a) The condensation of o-benzoquinone prepared from 0.75 g of pyrocatechol as described above with 2.0 g of 4-trifluoromethyl-o-phenylenediamine [10] yielded 0.12 g (10.7%) of 2-trifluoromethylphenazine. This forms pale yellow needles from alcohol, m.p. 177-178°.

b) A mixture of 0.35 g of 2-nitro-3'-trifluoromethyldiphenylamine and 0.7 g of charcoal was heated 10 minutes at 250-280°. The product was extracted with hot benzene, and the benzene solution was chromatographically separated on aluminum oxide. The lower pale yellow zone yielded 0.09 g (47%) of 2-trifluoromethylphenazine. This forms pale yellow needles from aqueous alcohol, m.p. 177-178°.

Found %: N 11.20, 11.06. $C_{13}H_7N_2F_3$. Calculated %: N 11.29.

0.13 g of unchanged 2-nitro-3'-trifluoromethyldiphenylamine was extracted from the upper zone.

A mixture of 2-trifluoromethylphenazine samples obtained by the first and second methods gave no melting point depression.

1-Methoxy-7-fluorophenazine. 15.3 g of o-nitroanisole, 11.1 g of p-fluoroaniline, and 20 g of caustic potash in 150 ml of benzene was taken for the reaction. The mixture was boiled 2 hours. Chromatographic separation of the condensation products yielded 0.46 g (2%) of 1-methoxy-7-fluorophenazine, m.p. 148-150°,

and 0.03 g of 1,7-dimethoxyphenazine, m.p. 147-150°. The latter gave no melting point depression with the 1,7-dimethoxyphenazine described earlier [13]. The 1-methoxy-7-fluorophenazine was twice crystallized from ligroine for analysis. It forms yellow needles, m.p. 150°. It dissolves in 15% hydrochloric acid with a red color.

Found %: N 12.25, 12.16. $C_{13}H_9ON_2F$. Calculated %: N 12.28.

In contrast to 1-methoxy-7-fluorophenazine, 1,7-dimethoxyphenazine dissolves in 15% hydrochloric acid with an orange color.

2-Trifluoromethylphenazine 9-oxide. A mixture of 9.6 g of m-nitrobenzo trifluoride, 4.65 g of aniline, 10 g of caustic potash, and 100 ml of benzene was boiled 20 hours. The reaction products yielded 0.15 g (1.1%) of small greenish yellow needles. The product was purified by crystallization from alcohol. It forms shiny yellow needles, m.p. 153°, decomp. 212-214°.

Found %: N 10.68, 10.74. $C_{13}H_7ON_2F_3$. Calculated %: 10.60

The reduction of 2-trifluoromethylphenazine yields a substance with m.p. 176-177° which gives no melting point depression with 2-trifluoromethylphenazine.

2-Trifluoromethylphenazine 10-oxide. a) A mixture of 6.15 g of nitrobenzene, 8.05 g of m-trifluoromethylaniline, 10 g of caustic potash, and 75 ml of benzene was boiled 10 hours. Separation of the reaction products yielded 0.18 g (1.4%) of 2-trifluoromethylphenazine 10-oxide in the form of greenish yellow leaflets with m.p. 163-165°. After recrystallization from alcohol the substance formed yellow leaflets, m.p. 165-166°, decomp. 226°.

Found %: N 10.41, 10.67. $C_{13}H_7ON_2F_3$. Calculated %: 10.60

Reduction of this substance also gave 2-trifluoromethylphenazine. Both N-oxides dissolve in 20% hydrochloric acid with a yellow color.

b) The separation of a mixture of phenazine derivatives obtained by boiling together 26 g of nitrobenzene, 17.5 g of m-trifluoromethylaniline, and 35 g of caustic potash in 150 ml of toluene yielded 0.11 g of 2-trifluoromethylphenazine with m.p. 173-175°, 0.08 g of phenazine with m.p. 173°, and 0.07 g of phenazine N-oxide which decomposes at 222°.

In addition to the above phenazine derivatives, the following substances were isolated as side products of the above alkaline condensations.

By the condensation of nitrobenzene with m-fluoroaniline: 3-fluoroazobenzene, 1.54 g (7.7%), orange needles from methanol, m.p. 47-48°.

Found %: N 13.99, 14.30. $C_{12}H_9N_2F$. Calculated %: N 14.00.

3-Fluoroazoxybenzene, 0.7 g (3.2%). Pale orange needles from methanol, m.p. 33-34°.

Found %: N 12.78, 13.11. $C_{12}H_9ON_2F$. Calculated %: N 12.96.

By the condensation of m-nitrofluorobenzene with aniline: 2-nitro-3'-fluorodiphenylamine, 5.52 g (23.2%), orange needles from methanol, m.p. 74-75°.

Found %: N 12.25, 12.18. $C_{12}H_9O_2N_2F$. Calculated %: N 12.07.

4-Nitro-3'-fluorodiphenylamine, 1.25 g (5.4%), orange-yellow needles from benzene, m.p. 128-129°.

Found %: N 11.96, 12.20. $C_{12}H_9O_2N_2F$. Calculated %: N 12.07.

By the condensation of nitrobenzene with p-fluoroaniline: 2-nitro-4'-fluorodiphenylamine, 1.2 g (5.2%), orangle needles from alcohol, m.p. 82-83°. A sample mixed with the product obtained by Vivian and Hartwell [2] gave no melting point depression.

4-Nitro-4'-fluorodiphenylamine, 0.5 g (2.1%), yellow needles from benzene, m.p. 191-192°. A sample mixed with the product synthesized by the reaction between p-nitrochlorobenzene and fluoroaniline gave no melting point depression.

Found %: N 12.28, 12.20. $C_{12}H_9O_2N_2F$. Calculated %: N 12.07.

4-Fluoroazobenzene (in small yield), orange-yellow needles from methanol, m.p. 81-82° (described in the literature, m.p. 82.5° [11]).

Found %: N 13.68, 13.84. $C_{12}H_9N_2F$. Calculated %: N 14.00.

By the condensation of o-nitroanisole with p-fluoroaniline: 3-methoxy-4-nitro-4'-fluorodiphenylamine, 0.37 g (1.4%), m.p. 137-140°, yellow needles from alcohol, m.p. 141-142°.

Found %: N 10.63, 10.44. $C_{13}H_{11}O_3N_2F$. Calculated %: N 10.68.

2-Nitro-4'-fluorodiphenylamine, 1.22 g (5.3%) m.p. 75-76°. Pale orange needles from ligroine, m.p. 81-82°; no melting point depression with the substance synthesized from o-nitrochlorobenzene and p-fluoroaniline.

2,2'-Dimethoxyazobenzene, 0.8 g, m.p. 75-78°. Pale yellow needles from methanol, m.p. 87-88°. A sample mixed with the substance prepared by Starke's method [14] gives no melting point depression.

2-Methoxy-4'-fluoroabenzene, 1.73 g (7.5%), red leaflets from methanol, m.p. 68-70°.

Found %: N 12.22, 12.30. $C_{13}H_{11}ON_2F$. Calculated %: N 12.17.

By the condensation of nitrobenzene with m-trifluoromethylaniline (Experiment "b"): 2-nitro-3'-trifluoromethyldiphenylamine, 0.92 g (3%), m.p. 60-62°. Brown prisms from ligroine, m.p. 66-67°.

Found %: N 10.05, 10.19. $C_{13}H_9O_2N_2F_3$. Calculated %: N 9.92.

This substance was used for cyclization into 2-trifluoromethylphenazine.

4-Nitro-3'-trifluoromethyldiphenylamine, 0.92 g (3%), m.p. 139-140°. Yellow needles from benzene-ligroine mixture, m.p. 145°.

Found %: N 9.91, 9.80. $C_{13}H_9O_2N_2F_3$. Calculated %: N 9.92.

3-Trifluoromethylazobenzene, 1.45 g (5.3%), m.p. 35-36°. Pale orange needles from methanol, m.p. 37°.

Found %: N 11.25. $C_{13}H_9N_2F_3$. Calculated %: N 11.20.

Azoxybenzene, 0.5 g (2.3%), m.p. 32-35°. Pale yellow needles from methanol, m.p. 37-38°. The substance was identified by a mixing test with azoxybenzene.

SUMMARY

1. By means of the alkaline condensation of aromatic nitro compounds with fluorine-containing aromatic amines, the following were prepared: 1-fluorophenazine, 2-fluorophenazine, 1-methoxy-7-fluorophenazine, 1-fluorophenazine 10-oxide, 2-trifluoromethylphenazine 10-oxide, and 2-trifluoromethylphenazine 9-oxide. With the exception of 2-fluorophenazine, these substances were prepared for the first time. 2-Fluorophenazine, and 1- and 2-trifluoromethylphenazine were also prepared by other methods.

2. Several fluorine-containing azo and azoxy compounds and o- and p-nitrodiphenylamines not described previously in the literature were isolated from the products of the alkaline condensation reactions.

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REACTIONS OF SODIUM ETHYL XANTHATE WITH PRIMARY β- AND δ-DIBROMIDES*

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By means of Chugaev's xanthate reaction [1] applied to a series of dihydric alcohols, as proposed by V. E. Tishchenko and A. F. Kosternaya [2], it was possible to bring about the transition from the corresponding α-glycol xanthate esters to hydrocarbonx of the C_nH_{2n-2} series of the acetylene and diene types.

For the preparation of glycol xanthate esters, Tishchenko and his school used Welde's method [3], which consists of the double decomposition reaction between α-dibromides and xanthates of alkali metals. In an attempt to prepare xanthate esters of secondary-tertiary and bitertiary α-glycols, we found that the reaction took an anomalous course [4]. It appeared of interest to extend Tishchenko's method to the preparation of xanthate esters of β- and δ-glycols.

Various glycol xanthate esters have been recommended as insecticides [5].

Trimethyleneglycol ethyl xanthate was prepared by the reaction between sodium ethyl xanthate and trimethylene dibromide:

$$C_2H_5OC(=S)SCH_2CH_2CH_2SC(=S)OC_2H_5$$

Pyrolysis of the ester yielded a small amount of a hydrocarbon which gave the double bond reaction.

Pentamethyleneglycol ethyl xanthate was prepared by the action of sodium ethyl xanthate on pentamethylene dibromide. In contrast to the crystalline isoamyl xanthate and benzyl xanthate esters of α-, β-, and δ-glycols [6], the ethyl xanthate esters of trimethylene- and pentamethyleneglycol are non-crystallizing oily substances which decompose during vacuum distillation.

EXPERIMENTAL

The action of sodium ethyl xanthate on trimethylene dibromide

After distillation the trimethylene dibromide had b.p. 164°, d_0^{18} 1.972.

Sodium ethyl xanthate was prepared by the action of carbon disulfide on an alcoholic solution of sodium ethoxide. The Na content of the recrystallized salt was 15.27% (calculated 15.96%).

57.6 g of the powdered xanthate, moistened by anhydrous alcohol to the thickness of a slurry, was placed in a flask fitted with a reflux condenser and mixed with 30.4 g of trimethylene dibromide. The flask was warmed several hours on the water bath at 40-50°. The fine crystalline precipitate of sodium bromide was separated from the liquid. Upon addition of water to the latter, a yellowish oil with an unpleasant odor separated out. After thorough washing with water it was dried by calcium chloride. The Beilstein test for halogens was negative. The yield of the ester was 34.6 g (88.6%).

The oil did not crystallize in freezing mixture, and did not distill under vacuum without decomposition (at 8 mm); analysis of the product dried over calcium chloride (d_0^0 1.238, d_0^{25} 1.2146) gave the following results.

Found %: S 45.13, 44.87 (carias). M 280.2, 278.6 (cryoscopically in benzene).
$C_9H_{16}O_2S_4$. Calculated %: S 45.09. M 264.36.

* A summary was published in Reports on the Scientific Work of Members of the D. I. Mendeleev All-Union Chemical Society, No. 2, p. 10 (1949).

The analytical data show that the substance is the ethyl xanthate ester of trimethylene glycol. To prove its structure, the ester was saponified by means of alcoholic alkali.

Action of alcoholic alkali on trimethyleneglycol ethyl xanthate. When the ester was mixed with alcoholic KOH solution, crystals were precipitated after several hours; after recrystallization from anhydrous alcohol, analysis upon combustion with H_2SO_4 gave the following results:

Found %: K 26.9. $C_3H_5O_2SK$. Calculated %: K 27.08.

The liquid alcohol layer gave a violet color with sodium nitroprusside and a white precipitate with mercuric chloride solution which, together with the odor, indicates the presence of a mercaptan, $HSCH_2CH_2CH_2SH$. The action of alcoholic alkali on trimethyleneglycol ethyl xanthate may be represented by the Equation:

$$C_2H_5OCSCH_2CH_2CH_2SCOC_2H_5 + 2KOH \rightarrow 2C_2H_5OCOSK + HSCH_2CH_2CH_2SH.$$

Thermal decomposition of trimethyleneglycol ethyl xanthate. 10 and 15 g respectively of trimethyleneglycol ethyl xanthate were heated in an apparatus described previously [4] on a Wood's alloy bath. At a bath temperature of 190 to 260° the substance distilled and gaseous products were evolved. A yellow liquid distilled from 190 to 230°, and a deep red liquid from 230 to 260°.

1250 ml of gas was collected in the first experiment, and 2200 ml in the second. Hydrogen sulfide in the gas was estimated by absorption in a pipet containing KOH solution, carbon oxysulfide by absorption in lead plumbite solution, and unsaturated hydrocarbons by absorption in bromine water. The gas had the following composition:

Name of gas	Yield (in %) Experiment I	Experiment II
Hydrogen sulfide	18.40	16.25
Carbon oxysulfide	75.31	70.65
Unsaturated hydrocarbon	6.23	13.27
	99.94	100.18

From the liquid distillate a fraction with b.p. 38°, which gave the mercaptan reaction, was obtained, and a number of high-boiling fractions with a revolting odor and extended boiling range.

In a separate experiment the hydrocarbon was purified to remove hydrogen sulfide and carbon oxysulfide, and tested for the presence of double and triple bonds. The hydrocarbon decolorized bromine water and alkaline $KMnO_4$ solution, and did not give a precipitate with ammoniacal silver oxide solution or with Ilosvay reagent. The qualitative reactions indicate the presence of a double and the absence of a triple bond in the hydrocarbon. Because of the small quantity available, the hydrocarbon was not studied in greater detail.

The action of sodium ethyl xanthate on pentamethylene dibromide. Pentamethylene dibromide was prepared by the heating of benzoylpiperidine with phosphorus pentabromide, by Braun's method [7]; b.p. 110° (at 22 mm), d_0^{19} 1.675.

55 g of the powdered xanthate, moistened with anhydrous ethyl alcohol, was mixed with 34.5 g of pentamethylene dibromide and warmed 4 hours in a round-bottomed flask under a reflux condenser on the water bath at 50-60°. After separation of the fine crystalline precipitate of sodium bromide, the liquid was treated with water.

A yellowish oil with a characteristic odor separated out. The yield of the product after washing and drying over calcium chloride was 3.69 g (77.28%); d_0^0 1.158. The Beilstein test for halogens was negative. The oil did not crystallize at −21°, and decomposed during vacuum distillation (at 8 mm).

Found %: S 39.45, 39.04. M 291.2, 287. $C_{12}H_{22}O_2S_4$. Calculated % S. 41.05. M 312, 396.

The rather low molecular weight and lower sulfur content in comparison with the theoretical values may be attributed to other directions of the reaction, accompanied by ring closure.

Action of alcoholic alkali on pentamethyleneglycol ethyl xanthate. When the ester was mixed with alcoholic KOH solution, crystals were deposited after some time, which after recrystallization gave analytical results similar to those described above for trimethyleneglycol ethyl xanthate. Mercaptan was qualitatively detected in the liquid by the reaction with mercuric chloride (white precipitate).

The action of alcoholic alkali on the ethyl xanthate ester yields a mixture:

$$2C_2H_5OCOSK + HSCH_2CH_2CH_2CH_2CH_2SH.$$

Thermal decomposition of pentamethyleneglycol ethyl xanthate. 6 g of the ester was heated in the apparatus described earlier, on a bath with Wood's alloy. Decomposition began at a bath temperature of 220-240°, and was completed at 300°.

500 ml of gas, and 4 g of liquid fractions boiling from 35 to 250°, was collected.

The gas burns with a bright yellow flame. Sulfur compounds give it a revolting odor. 98.03% of the gas was absorbed in a pipet containing KOH, and only 1.97% was absorbed by bromine water. It was not possible to determine the nature of the hydrocarbon absorbed by bromine water because of the low yield.

During fractionation of the liquid, about 1 g distilled below 100°, and the rest distilled between 100 and 250°, with the temperature rising steadily. Mercaptan was qualitatively detected in the first fraction. After treatment of this fraction with aqueous mercuric chloride solution a white precipitate was formed and a small layer separated out, which possibly contained a hydrocarbon which could not be investigated in greater detail because of the small quantity available.

SUMMARY

1. The action of sodium ethyl xanthate on trimethylene dibromide yields trimethyleneglycol ethyl xanthate.

2. The action of sodium ethyl xanthate on pentamethylene dibromide yields pentamethyleneglycol ethyl xanthate.

3. The xanthate esters of β- and δ-glycols decompose at higher temperatures than the xanthate esters of α-glycols; the decomposition is accompanied by the formation of small amounts of unsaturated hydrocarbons.

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THE ANOMALOUS REACTION OF α-HALO KETONES WITH TRIETHYL PHOSPHITE

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The reactions of α-halo ketones with phosphorous acid esters and salts of dialkyl phosphorous acids have been studied repeatedly with the aim of preparing ketophosphinic esters. Nylen [1] first attempted to synthesize the corresponding phosphonic ketones by means of the reaction between chloroacetone or ω-bromoacetone and sodium diethyl phosphite, but he was not successful in isolating the ketones.

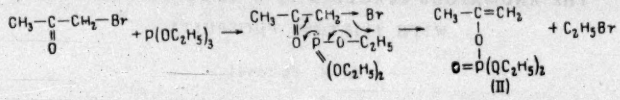
In 1934 A. E. Arbuzov and A. I. Razumov [2] showed that phosphonoacetophenone is formed by the action both of sodium diethyl phosphite and of triethyl phosphite on ω-bromoacetophenone. In 1946 A. I. Razumov and N. Petrov [3], by the action of triethyl phosphite on bromoacetone, obtained two products which agreed with phosphonoacetone in the analytical data for phosphorus, but which differed considerably from it in their physical constants and properties. These authors concluded that the substances they obtained were tautomeric forms of phosphonoacetone. In 1950, B. A. Arbuzov, B. P. Lugovkin, and N. P. Bogonostseva [4], in a study of the reaction between triethyl phosphite and α- and γ-bromoacetoacetic esters, showed that the phosphonoacetoacetic esters formed had very extended boiling temperature ranges. Upon saponification by hydrochloric acid the compounds decompose to form acetone and phosphoric acid. They also described the preparation of 2-diethylphosphonocyclohexanone by the action of triethyl phosphite on 2-chlorocyclohexanone and of sodium diethyl phosphite on 2-chloro- and 2-bromocyclohexanone. B. A. Arbuzov and V. S. Vinogradova [5] synthesized methylphosphonoacetone, dimethylphosphonoacetone, β-ketobutylphosphinic acid ester, methylphosphonoacetophenone and dimethylphosphonoacetophenone by the action of triethyl phosphite on the corresponding bromo ketones. From α-chlorocylopentanone and α-chloro-α-methylcyclopentanone and triethyl phosphite, α-phosphonocyclopentanone and α-phosphono-α-methylcyclohexanone were prepared. In view of our recent studies of the addition reactions between unsaturated compounds and dialkylphosphorous and dialkylthiophosphorus acids, the acid esters of ethyl- and phenylphosphinic acids, the ester and nitrile of phosphonoacetic acid, and their homologs, it was of interest to study analogous reactions with phosphonoacetone. The absence of exact data on the structure of phosphonoacetone in the literature led us to repeat the work of A. I. Razumov and N. Petrov and to study the substances obtained by them in greater detail; very interesting and somewhat unexpected results were obtained*.

According to A. I. Razumov and N. Petrov, the higher-boiling product (I) formed by the action of triethyl phosphite on bromoacetone reacts readily with sodium and does not form a semicarbazone; the lower-boiling product (II) reacts very weakly with sodium and with bromine, and forms a semicarbazone with m.p. 254°. Analytical data for the semicarbazone were not given. According to our experiments, (I) reacts vigorously with sodium, gives a very faint color with ferric chloride, and forms a phenylhydrazone with phenylhydrazine. Carbonyl group was determined quantitatively in (I). The compound (I) forms addition compounds with unsaturated compounds in the presence of sodium ethylate, and alkyl phosphonoacetones are formed by the action of alkyl halides on its potassium and sodium derivatives. On the basis of these experiments it was concluded that (I) is the keto form of phosphonoacetone:

$$CH_3COCH_2Br + P(OC_2H_5)_3 \longrightarrow \underset{(I)}{CH_3COCH_2}-P\begin{matrix}=O\\ \\ (OC_2H_5)_2\end{matrix} + C_2H_5Br.$$

* For preliminary data see Proc. Acad. Sci. USSR, 101, No. 5, 889 (1955).

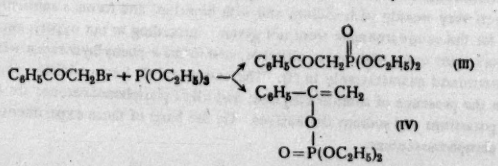
(II) does not react with sodium, vigorously adds on bromine, and gives no color with ferric chloride in alcohol solution. It does not form addition compounds with unsaturated compounds, or yield alkyl derivatives. An examination of the properties of (II) led to the conclusion that it is not a tautomeric form of phosphonoacetone, but is the diethylisopropenyl ester of phosphoric acid. The mechanism of its formation may be represented as follows. The presence of bromine in the methyl group of bromoacetone causes definite polarization of the molecule, which may lead to a considerable weakening of the nucleophilic properties of the oxygen atom. This makes possible an addition reaction between the phosphite ester and bromoacetone not only by A. E. Arbuzov's scheme, but also as the result of transfer of the reaction center to the carbonyl group oxygen:



Bromine may be split off in the anionic form during the reaction, but a more likely course is the simultaneous and gradual electron displacement in the molecules of both reagents by a cyclic mechanism, leading in the last analysis to the formation of ethyl bromide and an unsaturated phosphoric ester. An electronic displacement in the reverse direction is also possible, but in the present instance it appears less probable. Reesterification of (II) by means of ethyl alcohol in the presence of a small amount of sodium ethylate resulted in good yields of acetone and triethyl phosphate, identified by their constants and derivatives. Saponification of (II) by 30% sulfuric acid also yielded acetone. The reaction commenced when the reaction mixture was warmed to 50-60°, and subsequently was very vigorous and accompanied by much heat evolution and boiling of the reaction mixture. Temperature strongly influenced the proportions of (I) and (II) formed in the reaction between bromoacetone and triethyl phosphite. The content of (II) in the mixture of the products was higher as the reaction temperature was lower. When the reaction was carried out in ether solution, with a total yield of 66.3%, the content of (II) in the isomer mixture was 80.1%.

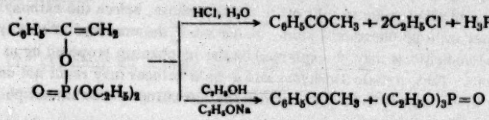
In order to confirm the proposed scheme for the reaction mechanism, it appeared of interest to study the reactions of triethyl phosphite with chloro- and iodoacetone. It might have been expected that increased polarization of the halogenated ketone molecule owing to the more electronegative chlorine would favor an anomalous reaction, while the lower polarizing effect of iodine would favor the normal reaction. In fact, when chloroacetone was used for the reaction at 120° and higher temperatures, (II) was obtained in good yield, while the reaction with iodoacetone in ether solution resulted in the formation of a mixture of (I) and (II) in 82.6% yield; the content of (I) in the mixture was 90%. It must be pointed out that our results differ from those reported in the literature [6] the formation only of (I) is described in the reaction between triethyl phosphite and chloroacetone at 160-165°. The reasons for this great difference between the results are not yet clear.

We also studied the reactions of triethyl phosphite with ω-chloro- ω-bromo-, and ω-iodoacetophenone. The reaction between triethyl phosphite and ω-bromoacetophenone was previously studied by A. E. Arbuzov and A. I. Razumov [2]. They isolated diacetylphosphonoacetophenone from the reaction products and established that it reacts with sodium. By a repetition of the experiment in analogous conditions we obtained a fraction which boiled in the range 182-193° (11 mm). Upon further distillation this yielded two products; phosphonoacetophenone (III), b.p. 192.5-193° (11 mm), and the α-phenylvinyldiethyl ester of phosphoric acid (IV), b.p. 171° (11 mm). The yield of (III) was about 6 times that of (IV), with a total 77% yield:



Saponification of (III) by means of dilute hydrochloric acid (1 : 1) at 140° during 4 hours gave acetophenonephosphinic acid, b.p. 143°, in 84% yield. When acetophenonephosphinic acid was heated 6 hours in dilute hydrochloric acid solution at 220°, it decomposed into acetophenone and phosphoric acid. The ability of

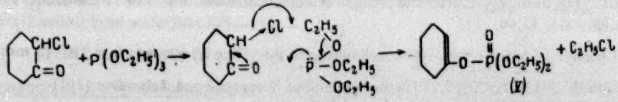
ketophosphinic esters to decompose into ketones and phosphoric acid on hydrolysis by hydrochloric acid was already noted previously by B. A. Arbuzov, Lugovkin, and Bogonostseva [4]. In the present instance there is an analogy between the behavior of benzoylacetic and acetophenonephosphinic acids; the latter, however, is much more stable. Benzoylacetic acid is hydrolyzed with the formation of acetophenone and carbon dioxide even during storage, and more rapidly on heating especially in the presence of mineral acids. This example once again confirms the deduction made by A. E. Arbuzov [7] concerning the analogy between the phosphon and carboxyl groups. When (III) is heated a short time in alcohol solution in the presence of a small amount of sodium ethylate, it is almost completely unchanged. Saponification of (IV) by dilute hydrochloric acid in conditions described previously for (III) gave acetophenone and phosphoric acid, while acetophenone was identified after re-esterification by means of ethyl alcohol.



The saponification of both esters by means of water at 100° was studied. The hydrolysis of (IV) is approximately 4-5 times as rapid as of (III), which is evidently the result of the much easier saponification of the α-phenylvinyl group in comparison with the ethyl group.

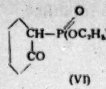
The proportions of (III) and (IV) formed in the reaction between triethyl phosphite and ω-haloacetophenones depends both on the temperature conditions and on the nature of the halogen. The reaction with bromoacetophenone in ether solution gave a mixture of both isomers, in which (III) comprised not 85% (see previous experiment) but only 64%. As the result of the reaction with iodoacetophenone, also in ether, 76% of (III) was present in the isomer mixture; only (IV) was obtained in the reaction with chloroacetophenone. There is thus an analogy between the reactions of haloacetones and ω-haloacetophenones with triethyl phosphite, which serves as confirmation of the validity of our conclusion concerning the effect of polarization of the halo ketone molecule on the reaction mechanism.

Finally, the reactions of triethyl phosphite and sodium diethyl phosphite with 2-dichlorocyclohexanone were studied. The action of triethyl phosphite on 2-chlorocyclohexanone yielded only one product, (V), with b.p. 143° (13 mm), n_D^{20} 1.4523, d_4^{20} 1.1032 and 88 % yield. According to N. P. Bogonostseva [4], it has b.p. 160-163° (17 mm), n_D^{20} 1.4510, d_0^0 1.1234; on saponification by dilute hydrochloric acid it follows that the yielded product decomposes into cyclohexanone and phosphoric acid. According to our experiments, re-esterification of (V) with ethyl alcohol in the presence of sodium ethylate very readily and quantitatively yields cyclohexanone and triethyl phosphite, it reacts very weakly with sodium, and bromination by McIlhiney's method (half-hour standing with bromine at room temperature) showed the presence of 87% double bonds. Our data, in conjunction with the hydrolysis results obtained by N. P. Bogoslovskaya, indicate that (V) is the cyclohexenyl diethyl ester of phosphoric acid. Consequently, the reaction between chlorocyclohexanone and triethyl phosphite occurs completely by an anomalous mechanism.



The action of sodium diethyl phosphite on 2-chlorocyclohexanone gave the product (VI), b.p. 146-146.5° (11 mm), n_D^{20} 1.4576, d_4^{20} 1.1252, that is, somewhat different in its physical constants from (V). The hydrolysis of (VI) by dilute hydrochloric acid resulted in the formation of ethyl chloride and a non-crystallizing acid; after this was heated a short time in alcohol solution in the presence of a small amount of sodium ethylate most of it distilled unchanged; titration by McIlhiney's method (half-hour standing with bromine at room temperature) showed about 15% double bonds; it reacted rather sluggishly with sodium. Study of the hydrolysis kinetics of (V) and (VI) by distilled water at 100° showed that (VI) is saponified 4-5 times as slowly as (V). From these results

it may be concluded that (VI) is a cyclohexanonephosphinic ester, or the product of the normal reaction between sodium diethyl phosphite and chlorocyclohexanone. The double bond shown in (VI) by bromine titration is evidently to be attributed to the enol form present; its content may increase in the course of the analysis. A cyclohexanonephosphinic ester (VI) with similar physical constants (b.p. 148-149° (11.5 mm), n_D^{20} 1.4578, d_0^0 1.1270) was previously prepared by N. P. Bogonostseva by the action of sodium diethyl phosphite on bromocyclohexanone [4].



(VI)

In the course of the present investigation the author became acquainted with Perkow's work on the action of triethyl phosphite on chloral and bromal [8]. Perkow showed, by studies of hydrolysis and chlorination reactions and by negative aldehyde group reactions, that the substances obtained by him are β,β-dihalovinyl diethyl esters of phosphoric acid. He did not propose a reaction mechanism, but merely put forward the view that the halogenated alkyl group is split off in the first phase, before the carbonyl group oxygen combines with the phosphorus atom. In our view, the reactions of triethyl phosphite with bromal and chloral may be explained by the mechanism proposed by us for the anomalous α-halo ketone reactions. Thus, α-halo aldehydes and α-halo ketones may react not only according to the Arbuzov rearrangement, but by an anomalous mechanism, with the formation of unsaturated phosphate esters.

EXPERIMENTAL*

Action of triethyl phosphite on chloroacetone. 18.5 g of chloroacetone was added dropwise to 35 g of triethyl phosphite in an Arbuzov flask heated to 120°. The reaction mixture was then heated 1 hour at 160° and distilled under vacuum. The yield was 22.8 g of diethyl isopropenyl phosphate.

B.p. 96° (12 mm), n_D^{20} 1.4190, d_4^{20} 1.0708, MR_D 45.80; calc. 46.05.

Found %: C 43.37; H 7.83; P 16.08. $C_7H_{15}O_4P$. Calculated %: C 42.89; H 7.72; P 15.97.

Re-esterification of diethyl isopropenyl phosphate. A solution of sodium ethylate was prepared in an Arbuzov flask fitted with a downward condenser from 0.2 g of sodium and 15 ml of anhydrous ethyl alcohol. After the addition of 10 g of diethyl isopropenyl phosphate, the reaction mixture was heated on the water bath. 1.65 g of acetone, b.p. 56.5-58°, was distilled off. The semicarbazone had m.p. 186-187° (mixed m.p. sample). Distillation of the residue yielded 8.45 g of triethyl phosphate, b.p. 74° (3.5 mm), n_D^{20} 1.4065, d_4^{20} 1.0694. According to [9], it has b.p. 75.5° (5 mm), n_D^{20} 1.4053, d_4^{20} 1.0695.

Saponification of diethyl isopropenyl phosphate. 10 g of the ester was heated with 15 ml of 30% sulfuric acid in an Arbuzov flask fitted with a downward condenser. The saponification was very turbulent, with much evolution of heat and rapid distillation of acetone. 2.8 g of acetone was collected, b.p. 56.5-57°, semicarbazone m.p. 187°. After removal of the alcohol the residue was diluted to 50 ml with water, and the phosphoric acid content of 1 ml was determined by Neumann's method. H_3PO_4 found, 0.1006 g. Calculated 0.1010 g.

Action of triethyl phosphite on bromoacetone. Experiment 1. The reaction was carried out with 93 g of triethyl phosphite and 76.9 g of bromoacetone at 110-120°. After addition of the bromoacetone the mixture was heated 1 hour at 150-170° and then distilled under vacuum. The yield was 15 g of diethyl isopropenyl phosphate, b.p. 99-102° (15 mm), n_D^{20} 1.4190 and 75 g of phosphonoacetone, b.p. 126° (9 mm), n_D^{20} 1.4350, d_4^{20} 1.1252, MR_D 44.98; calc. 45.40.

The action of phenylhydrazine on phosphonoacetone gave the phenylhydrazone, b.p. 193° (3 mm).

Found %: P 11.27; CO 13.76 (by the method of Terentyev and Zahrodina [10]). $C_{13}H_{21}O_3N_2P$. Calculated %: P 10.91; CO 14.23.

Experiment 2. The reaction was carried out with 31 g of triethyl phosphite and 25.6 g of bromoacetone in 50 ml of ether. The ether solution was heated 2 hours on the water bath. The yield was 4.6 g of phosphonoacetone and 18.6 g of diethyl isopropenyl phosphate.

* N. M. Lebedeva participated in the experiments on the reactions between chloro- and bromoacetone and triethyl phosphite.

Action of triethyl phosphite on iodoacetone. 41 g of iodoacetone was added to a solution of 40 g of triethyl phosphite in 100 ml of anhydrous ether. The reaction mixture was heated 1 hour on the water bath. The yield was 33 g of phosphonoacetone, 2.7 g of diethyl isopropenyl phosphate, and 2.2 g of diethylphosphorous acid.

Action of triethyl phosphite on ω-bromoacetophenone. Experiment 1. 46.5 g of ω-bromoacetophenone was added dropwise to 40 g of triethyl phosphite and 25 ml of dry benzene. 10-15 minutes after the addition of the whole amount of ω-bromoacetophenone, the temperature of the reaction mixture began to rise, and then to boil violently; the temperature of the liquid rose to 150°. At the end of the reaction, the reaction mixture was heated 0.5 hour on the water bath and distilled under vacuum. After several distillation with the use of a small column, 34.7 g of diethylphosphonoacetophenone (III) and 6.1 g of α-phenylvinyl diethyl phosphate (IV) was obtained.

(III) B.p. 192-192.5° (11 mm), n_D^{20} 1.5137, d_4^{20} 1.1790, MR_D 65.3; calc. 64.9.

(IV) B.p. 171° (11 mm), n_D^{20} 1.5009, d_4^{20} 1.1422, MR_D 66.0; calc. 65.5.

Found % P 12.44, 12.16. $C_{12}H_{17}O_4P$. Calculated % P 12.11.

Experiment 2. The reaction was carried out by heating 32 g of ω-bromoacetophenone, 30 g of triethyl phosphite, and 100 ml of dry ether 2 hours on the water bath. The yield was 24.6 g of diethylphosphonoacetophenone and 13.8 g of α-phenylvinyl diethyl phosphate.

Action of triethyl phosphite on ω-chloroacetophenone. 23.1 g of chloroacetophenone was added gradually to 25.1 g of triethyl phosphite. The reaction started when the temperature of the reaction mixture rose to 100°; upon further addition the temperature rose to 130-140°. It was kept at this level until all of the chloroacetophenone had been added. The mixture was heated half an hour at 140° and then distilled under vacuum. The yield was 34.6 g of α-phenylvinyl diethyl phosphate, b.p. 172° at 12 mm, n_D^{20} 1.5020. The residue weighed 2.5 g.

Action of triethyl phosphite on ω-iodoacetophenone. The reaction was carried out by heating 25 g of ω-iodoacetophenone, 25 g of triethyl phosphite and 100 ml of ether 2 hours on the water bath. The yield was 14 g of phosphonoacetophenone and 4.5 g of α-phenylvinyl diethyl phosphate.

Re-esterification of α-phenylvinyl diethyl phosphate. 4 g of the phosphate ester was added to an alcohol solution of sodium ethylate prepared from 0.2 g of sodium and 20 ml of anhydrous ethanol. The alcohol was slowly distilled off out of an Arbuzov flask, and the residue distilled under vacuum. 2.3 g of a fraction with b.p. 96-98°(20 mm) was obtained. The residue in the flask began to decompose during further distillation. Treatment of the fraction collected with semicarbazide, gave a semicarbazone, m.p. 198-198.5° (after three recrystallizations from alcohol, mixed sample melting point test).

In an analogous experiment with phosphonoacetophenone, the latter was obtained back almost completely from the reaction medium without change.

Saponification of diethylphosphonoacetophenone. 10 g of diethylphosphonacetophenone was heated with 20 ml of dilute hydrochloric acid (1:1) in a sealed tube 3-4 hours at 140°. The upper layer was transferred to a flask, and careful distillation on the water bath yielded only ethyl chloride. No high-boiling residue remained. By repeated evaporation of the lower layer with distilled water, 6.5 g of acetophenonephosphinic acid, m.p. 143° (recrystallization from water)was obtained.

Found % P 16.05, 15.59. $C_8H_9O_4P$. Calculated % P 15.50.

Decomposition of acetophenonephosphinic acid. 6 g of acetophenonephosphinic acid and 15 ml of dilute hydrochloric acid (1:1) was heated in a sealed tube 6 hours at 220-230°. The liquid separated into two layers. The upper layer, after ether extraction and distillation, yielded 1 g of acetophenone, b.p. 80-81° (11 mm), n_D^{20} 1.5309. After removal of hydrogen chloride from the lower layer (by repeated evaporation with distilled water), 2.9 g of phenylhydrazine phosphate was precipitated by the addition of phenylhydrazine. After several recrystallizations from alcohol it melted at 154-155° with swelling. No. melting point depression was given by a mixed sample.

Saponification of α-phenylvinyl diethyl phosphate. 15.5 g of the phosphate ester and 30 ml of dilute hydrochloric acid was used in the saponification. Some evolution of heat was already observed when the

TABLE 1

Time from start of experiment (hours)	Amount of 0.01 N KOH solution (in ml) for titration after saponification	
	phosphonacetone	phosphate ester
1	1.8	9.1
2	2.8	13.5
4	4.3	21.6
6	6.1	29.2
7	6.9	32.4
10	8.5	37.3
13	9.3	41.5
16	10.4	43.8
20	11.2	45.2

TABLE 2

Time from start of experiment (hours)	Amount of 0.01 N KOH solution (in ml) for titration after saponification	
	phosphonocyclohexanone	phosphate ester
0	0.4	1.6
1	1.3	5.8
3	2.0	8.5
4	–	9.9
5	2.8	–
6	–	11.3
7	3.7	–
9	4.0	14.5
12	4.2	–
13	–	21.6
17	4.3	–
18	–	28.2
19	5.8	–
22	–	32.0
24	72.	–

liquids were mixed in the tube. The heating was continued 4 hours at 140°. The upper layer yielded 5.6 g of acetophenone with b.p. 199-201°, n_D^{20} 1.5307. The semicarbazone had m.p. 197-198° (mixed sample). Phenylhydrazine was added to the lower layer after complete removal of hydrogen chloride (evaporation with water in a basin and distillation under vacuum). After recrystallization from water and alcohol the phenylhydrazine phosphate had m.p. 155-156° (mixed sample).

Saponification kinetics of phosphonoacetophenone and α-phenylvinyl diethyl phosphate. The saponification was carried out in 30% aqueous alcohol solution at 100° in glass ampoules. The concentration of the esters being saponified was 0.004 molar.

The acid esters formed by the saponification were titrated with 0.01 N caustic potash solution (Table 1).

Action of triethyl phosphite on 2-chlorocyclohexanone. 13.2 g of chlorocyclohexanone and 16.6 g of triethyl phosphite were heated on a water bath in a flask fitted with a distillation column connected to a downward condenser. When the bath temperature reached 70°, ethyl chloride began to evolve from the reaction mixture. The temperature of the reaction mixture quickly rose to 140° and remained at this level 10-15 minutes. The flask was then heated on an oil bath at 160-170° 30 minutes. The yield was 20.7 g of cyclohexenyl diethyl phosphate.

B.p. 143° (11 mm), n_D^{20} 1.4523, d_4^{20} 1.1032, MR_D 57.3; calc. 57.7.

Found %: P 13.52. $C_{10}H_{19}O_4P$. Calculated %: P 13.24. McIlhiney double bond test: 0.68 g sub.; bromine added, 0.40 g. Calculated 0.46 g.

Re-esterification of cyclohexenyl diethyl phosphate. 10 g of the phosphate ester was added to a solution of sodium ethylate prepared from 0.1 g of sodium and 10 ml of anhydrous ethyl alcohol. The ethyl alcohol was distilled from the reaction mixture through a small Widmer column, and the residue was distilled under vacuum. The yield was 2.6 g of cyclohexanone with b.p. 46-47° (15 mm), 153-154° (750 mm), n_D^{20} 1.4503. The semicarbazone had m.p. 165-166° (mixed sample); and 6 g of triethyl phosphate, b.p. 97-98° (15 mm), n_D^{20} 1.4067, d_4^{20} 1.0690 was also obtained. The triethyl phosphate was saponified by dilute hydrochloric acid at 140°. The liquid separated into two layers. The upper layer consisted of ethyl chloride. After complete removal of hydrogen chloride (by repeated evaporation), phenylhydrazine phosphate was obtained from the aqueous layer by the addition of phenylhydrazine. After several recrystallizations from alcohol it had m.p. 154-156°.

Action of sodium diethyl phosphite on chlorocyclohexanone. 23 g of chlorocyclohexanone was added to an ether solution of sodium diethyl phosphite, prepared from 3.8 g of sodium and 25 g of diethylphosphorous acid. The reaction mass was heated 3 hours, and sodium chloride which was precipitated in the colloidal state was separated by centrifugation. Distillation of the residue yielded 25.5 g of the diethyl ester of cyclohexanonephosphinic acid.

B.p. 126° (3 mm), 146-146.5° (11 mm), n_D^{20} 1.4576, d_4^{20} 1.1252, MR_D 56.71; calc. 57.05.
Found % P 13.13, 13.26. $C_{10}H_{19}O_4P$. Calculated % P. 13.24. McIlhiney bromination test (sample stood 30-40 min. at room temperature), 0.57 g subs; bromine added, 0.06 g.

Saponification of the diethyl ester of cyclohexanonephosphinic acid. 6.2 g of the ester was heated with 15 ml of dilute hydrochloric acid (1:1) 4 hours at 140°. The liquid separated into two layers. The upper layer consisted of ethyl chloride. The small residue (0.6 g) which remained in the flask after removal of the ethyl chloride was added to semicarbazide solution. No semicarbazone was formed. The aqueous layer was carefully evaporated after removal of hydrogen chloride. The residue was a thick yellow liquid which did not crystallize on standing.

Saponification kinetics of cyclohexanonephosphinic ester and of cyclohexenyl diethyl phosphate. The saponification was carried out in 30% aqueous alcohol solution at 100° in glass ampoules. The ester concentration was 0.004 molar. The acid esters formed were titrated with 0.01 N caustic potash solution (Table 2).

SUMMARY

1. An anomalous reaction between triethyl phosphite and α-halo ketones: α-chloro-, α-bromo-, and α-iodoacetone, ω-chloro-, ω-bromo-, and ω-iodoacetophenone, and chlorocyclohexanone, which leads to the formation of unsaturated phosphoric acid esters, has been discovered and studied.

2. The temperature and the nature of the halogen have a significant influence on the course of the reaction between halo ketones and triethyl phosphite. The lower the temperature at which the reaction is performed, the higher is the yield of the anomalous product – unsaturated phosphate ester. The influence of the nature of the halogen is apparently associated with its polarizing effect on the halo ketone molecule. In the case of chloro ketones the reaction proceeds mainly by the anomalous mechanism, with bromo ketones it proceeds in both directions, and with iodo ketones mainly by the normal scheme (according to the Arbuzov rearrangement).

3. A mechanism of the anomalous reaction of halo ketones with triethyl phosphite has been put forward.

The author expresses his gratitude to B. A. Arbuzov for his interest in the work and for discussion of the results.

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* T.p. = C. B. translation pagination.

INVESTIGATIONS OF THE IMIDAZOLE SERIES

I. 4 (5) -PHENYLIMIDE-AZOLYL-2-MERCAPTANS AND SULFIDES

P. M. Kochergin and M. N. Shchukina

For sulfone synthesis in the imidazole series it appeared of interest to prepare 4(5)-phenyl-, 4 (5)-p--nitrophenyl-, and 4 (5)-p-aminophenyl-2-mercaptoimidazoles, and to study their alkylation and arylation reactions. Although 4 (5)-phenyl-2-mercaptoimidazole has long been known [1-3], its p-nitro and p-amino derivatives have not been described, and of its own derivaties only the S-benzyl derivative [3] and some N-substituted and N,S-disubstituted products are known [3, 4]. 4(5)-phenyl- and 4(5)-p-nitrophenyl-2-mercaptoimidazole were prepared from acetophenone and p-nitroacetophenone respectively through the α-bromo ketones, their urotropine complexes, the α-amino ketone hydrochlorides, by condensation of the latter with potassium thiocyanate. It was found that when the reaction takes place in aqueous solution, the formation of the corresponding 2-mercaptoimidazoles is accompanied by partial hydrolysis of the α-amino ketone hydrochlorides and their condensation to dihydropyrazine derivatives, which are readily oxidized by atmospheric oxygen to pyrazine derivatives. For example, when α-aminoacetophenone hydrochloride reacts with potassium thiocyanate in aqueous solution in the conditions described by Grant and Pyman [1], in addition to 4 (5)-phenyl-2-mercaptoimidazole we obtained 2,5-diphenylpyrazine [6] (yield about 1.5-3%). The condensation of α-amino-p-nitroacetophenone hydrochloride [7] with potassium thiocyanate in aqueous solution at 100° and lower temperatures does not give 4 (5)-p-nitrophenyl-2-mercaptoimidazole in the pure state, but a brown amorphous powder is formed. Oxidation of this powder by nitric acid [8] gave 4 (5)-p-nitrophenylimidazole in a yield which indicated that the original material did not contain more than 30-33% of the corresponding mercaptoimidazole. The preparation of 4 (5)-phenyl- and 4 (5)-p-nitrophenyl-2-mercaptoimidazoles proceeds more smoothly in non-aqueous solvents. Thus, the condensation of α-aminoacetophenone hydrochloride with potassium thiocyanate in anhydrous ethyl alcohol or glacial acetic acid gave 4 (5)-phenyl-2-mercaptoimidazole in 80% yield and in a purer state than from aqueous solution. By an analogous method we prepared 4 (5)-p-nitrophenyl-2-mercaptoimidazole from α-amino-p-nitroacetophenone in anhydrous methyl alcohol or glacial acetic acid solution in yields of 89 and 98% respectively. To prove its structure, this substance was oxidized by means of nitric acid to 4 (5)-p-nitrophenylimidazole [1]. 4 (5)-p-Aminophenyl 2-mercaptoimidazole was prepared by the reduction of 4 (5)-p-nitrophenyl-2-mercaptoimidazole with hydrogen sulfide in alcohol -ammonia solution [1].

S-alkyl (aryl) derivatives of 4 (5)-phenyl- and 4(5)-p-nitrophenyl-2-mercaptoimidazoles were prepared by the action of alkyl and aryl halides (in equimolecular amounts) on mercaptoimidazoles in alcohol solution in the presence of the equivalent amount of alkali. By the action of 2 moles of ethyl iodide on 4(5)-phenyl--2-mercaptoimidazole in alcohol solution in the presence of two equivalents of alkali the formation of two isomers can be expected: 4-phenyl- and 5-phenyl-1-ethyl-2-ethylmercaptoimidazole. We only obtained one substance by means of this reaction, which was apparently 1-ethyl-4-phenyl-2-ethylmercaptoimidazole, by analogy with the fact that 4(5)-phenyl-2-benzylmercaptoimidazole also forms only one isomer on methylation in alcohol solution in the presence of alkali – 1-methyl-4-phenyl-2-benzylmercaptoimidazole [4].

The compounds obtained, with the exception of 4(5)-p-aminophenyl-2-mercaptoimidazole, were tested in the Chemotherapy Department of the All-Union Scientific Research Institute for Pharmaceutical Chemistry for antibacterial activity (a range of 16 species of microorganisms)*. The Table shows the dilutions of the products at which complete inhibition of bacterial growth in vitro was found (10 species). 4 (5)-Phenyl-2-p--nitrophenylmercaptoimidazole was inactive. All the compounds were inactive toward the enteric,

* The tests were carried out by S. N. Milovanova and O. O. Makeeva under the guidance of G. N. Pershin.

Antibacterial Activity of the Compounds with the General Formula

Serial No.	R	R'	R''	Activity against microorganisms								
				Staphylococcus aureus	Hemolytic streptococcus	pneumococcus	anthracoid spores	human tuberculosis bacillus	avian tuberculosis bacillus	acid-resistant saprophyte B_5	microsporon	trichophyton	achorion
1	NO_2	H	H	1 : 2000	* 0	1 : 2000	0	0	0	0	1 : 1000	1 : 1000	0
2	NO_2	H	C_6H_{11}**	1 : 8000	1 : 4000	1 : 8000	1 : 8000	1 : 32000	1 : 64000	1 : 64000	1 : 16000	1 : 16000	1 : 16000
3	H	C_2H_5	C_2H_5	1 : 4000	1 : 4000	1 : 4000	1 : 2000	1 : 2000	1 : 8000	1 : 4000	1 : 8000	1 : 8000	1 : 8000
4	H	H	CH_3	0	0	0	0	1 : 8000	1 : 8000	1 : 4000	1 : 4000	1 : 8000	1 : 16000
5	H	H	C_2H_5	0	0	0	0	1 : 16000	1 : 8000	1 : 16000	1 : 8000	1 : 4000	1 : 16000
6	H	H	C_4H_9**	0	0	0	0	1 : 16000	1 : 4000	1 : 8000	1 : 2000	1 : 2000	1 : 4000
7	H	H	C_4H_9**	1 : 4000	1 : 2000	1 : 8000	1 : 4000	1 : 64000	1 : 32000	1 : 16000	1 : 16000	1 : 16000	1 : 16000
8	H	H	C_5H_{11}**	1 : 2000	1 : 2000	1 : 2000	1 : 4000	1 : 128000***	1 : 64000	1 : 32000	1 : 16000	1 : 16000	1 : 16000
9	H	H	C_6H_{13}**	1 : 4000	1 : 2000	1 : 2000	1 : 2000	1 : 512000***	1 : 128000	1 : 64000	1 : 8000	1 : 16000	1 : 16000

* 0 – absence of activity.

** Tested as hydrochlorides.

*** In the presence of normal horse serum 1 : 16000.

enterotyphoid, Flechsner's dysenteric, diphtherial (strain PW_8) and pyocyaneus bacilli, with the exception of 4 (5)-p--nitrophenyl-2-isoamyl- and 4-ethyl--4-phenyl-2-ethylmercaptoimidazoles, which showed slight activity against the diphtheria bacillus and Proteus vulgaris. Their highest activity was against the tuberculosis bacillus, and their activity, as is the case in other classes [9], increases with the length of the alkyl chain. The activity of 4 (5)-phenyl-2-alkylmercaptoimidazoles falls sharply in the presence of serum.

EXPERIMENTAL

I. 4 (5)-Phenyl-2-Mercaptoimidazole. A solution of 28 g of α-aminoacetophenone hydrochloride and 17.6 g of potassium thiocyanate in 120 ml of anhydrous alcohol was boiled 3.5 hours. The precipitate which separated on cooling was filtered off, washed with a small amount of alcohol, then with water, and dried. The yield was 16 g of slightly greenish crystalls with m.p. 259-260°. Evaporation of the alcohol mother liquor to a small volume yielded a further 7 g of a substance with m.p. 254-256°. After recrystallization from alcohol-benzene mixture (4:1), 4(5)-phenyl-2-mercaptomidazole had m.p 261°.

When the reaction was performed in glacial acetic acid (50 ml, 2 hours heating at 100°), 4 g of α-aminoacetophenone hydrochloride and 2.5 g of potassium thiocyanate yielded 3.3 g of 4 (5)-phenyl--2-mercaptoimidazole (m.p. 261°; yield 80.5%).

II. 4(5)-p-Nitrophenyl-2-mercaptoimidazole. A solution of 4.6 g of α-amino--p-nitroacetophenone hydrochloride and 2.5 g of potassium thiocyanate in 100 ml of anhydrous methyl alcohol was boiled 2 hours; a yellow precipitate was formed which was, after cooling of the mixture, filtered off, washed with water, and dried. Evaporation of the alcohol mother liquor yielded another portion

of this substance. The total yield was 4.2 g of 4 (5)-p-nitrophenyl-2-mercaptoimidazole (yield 89.3%); this forms long yellow needles from glacial acetic acid, which darken at 240° and do not melt at 320°; the substance dissolves with difficulty in alcohol, acetone, glacial acetic acid, and mineral acid solutions, and is almost insoluble in most other organic solvents and in water; with strong alkalies it forms a deep violet solution. The substance decolorizes 0.1 N alcoholic iodine solution and gives a reddish brown color with ferric chloride solution. The hydrochloride and picrate of 4 (5)-p-nitrophenyl-2-mercaptoimidazole are hydrolyzed in alcohol.

When the reaction was carried out in glacial acetic acid (140 ml, heated 2 hours at 100°), 8 g of α-amino-p-nitroacetophenone hydrochloride and 4.3 g of potassium thiocyanate yielded 8 g of 4 (5)-p-nitrophenyl-2-mercaptoimidazole (yield 98%).

Found %: C 48.50; H 3.25; N 18.89; S 14.24. $C_9H_7O_2N_3S$. Calculated %: C 48.84; H 3.19; N 19.00; S 14.19*.

III. 4 (5)-p-Nitrophenylimidazole. To 17 ml of 10% nitric acid heated on a boiling water bath, 1.0 g of 4(5)-p-nitrophenyl-2-mercaptoimidazole was added in small portions during 7-10 minutes, and the mixture was then heated a further 15 minutes. The solution was then cooled, and the precipitate filtered off and washed with 10 ml of cold water. A further 0.1 g of pale yellow needles with m.p. 197-199°; after recrystallization from alcohol, 4 (5)-p-nitrophenylimidazole nitrate had m.p. 200°. The base, 4 (5) p-nitrophenylimidazole, forms yellow needles from alcohol, m.p. 225°.

IV. 4(5)-p-Aminophenyl-2-mercaptoimidazole. Hydrogen sulfide was passed through a solution of 6 g of 4 (5)-p-nitrophenyl-2-mercaptoimidazole in 400 ml of alcohol and 50 ml of aqueous ammonia (d 0.92) 10 hours at room temperature. The red-brown solution was then heated at the boil 1 hour and evaporated to dryness under vacuum. The dry residue was treated with boiling acetone, cooled and filtered. The acetone solution was evaporated to dryness under vacuum, and the residue was dried in a vacuum desiccator. The yield was 5.0 g of a substance which decomposed at 210-230°. For analysis, 4 (5)-p-aminophenyl-2-mercaptoimidazole was repeatedly recrystallized from alcohol: it forms slightly brownish crystals, darkens at 220°, melts at 237-239°, is easily soluble in acetone, alcohol, glacial acetic acid, hydrochloric acid and solutions of alkalies, dissolves with very great difficulty in ether, chloroform, carbon tetrachloride, dioxane, ethyl acetate, toluene, and ligroine, and is insoluble in water.

Found %: C 56.66; H 4.92; N 21.36; S 16.60. $C_9H_9N_3S$. Calculated %: C 56.49 H 4.75; N 21.98; S 16.77.

The hydrochloride forms brownish crystals, darkens at 240°, decomposes at 260-270°; is easily soluble in water, and with difficulty in alcohol.

Found %: Cl 15.60. $C_9H_{10}N_3SCl$. Calculated %: Cl 15.58.

V. 4 (5)-Phenyl-2-methylmercaptoimidazole. To a solution prepared from 0.33 g of metallic sodium and 18 ml of alcohol, 5 ml of water and 2.52 g of 4 (5)-phenylmercaptoimidazole was added. When this dissolved, 2.13 g of methyl iodide was added and the solution was heated on the water bath 4 hours at 43-45°, and then at the boil 10-15 minutes. At the end of the reaction (medium neutral to litmus) the solvent was driven off under vacuum, water was added to the residue, and the oily substance which separated was extracted with ether. The ether solution was dried over sodium sulfate and then evaporated to dryness under vacuum. The yield was 2.65 g of a substance with m.p. 132-133° (yield 97.5%). 4 (5)-Phenyl-2-methylmercaptoimidazole forms colorless crystals (from 60% alcohol) with m.p. 135.5-136.5°, easily soluble in most organic solvents, mineral acids, and alkali solutions on heating, insoluble in water.

Found %: C 62.88; H 5.62; N 14.65; S 17.08. $C_{10}H_{10}N_2S$. Calculated %: C 63.10; H 5.30; N 14.73; S 16.86.

The hydrochloride forms colorless long needles from alcohol, m.p. 189-191°; soluble in alcohol, acetone and water.

Found %: Cl 15.54. $C_{10}H_{11}N_2SCl$. Calculated %: Cl 15.65.

* All the analyses were performed in the Microanalytical Laboratory of the All-Union Scientific Research Institute for Pharmaceutical Chemistry, under the guidance of V. V. Kolpakova.

VI. 4(5)-Phenyl-2-ethylmercaptoimidazole. This was prepared analogously to (V) from 2.8 g of 4(5)-pehnyl-2-mercaptoimidazole and 2.73 g of ethyl iodide in an alkaline solution prepared from 0.36 g of metallic sodium, 14 ml of alcohol, and 5 ml of water. The heating was continued 2 hours at 65-70°, then 30 minutes at the boiling point of the solution. The yield of substance with m.p. 126-127° was 3.15 g (97.1%). 4(5)-Phenyl-2-ethylmercaptoimidazole consists of long colorless needles (from aqueous alcohol) m.p. 129-130°, easily soluble in most organic solvents, mineral acid solutions and caustic alkali solutions on heating; soluble with difficulty in ether and carbon tetrachloride; insoluble in cold water and ligroine.

Found %: C 64.78; H 5.77; N 13.42; S 15.94. $C_{11}H_{12}N_2S$. Calculated %: C 64.65; H 5.92; N 13.72; S 15.70.

The hydrochloride forms long colorless needles from alcohol, m.p. 62-63°, soluble in alcohols, acetone, and water.

Found %: Cl 14.51. $X_{11}H_{13}N_2SCl$. Calculated %: Cl 14.73.

VII. 4(5)-Phenyl-2-n-propylmercaptoimidazole. This was prepared analogously to (V) by the alkylation of 2.9 g of 4(5)-phenyl-2-mercaptoimidazole by normal propyl bromide (2.29 g) in an alkaline solution prepared from 0.38 g of metallic sodium, 14 ml of alcohol, and 5 ml of water. The solution was heated 2 hours at 35-37°, then 1 hour at 55-60°, and 1 hour at the boil. The yield of substance with m.p. 73-75° was 3.65 g (98.5%).

4(5)-Phenyl-2-n-propylmercaptoimidazole forms colorless needles (from aqueous acetone), m.p. 78-79°, is easily soluble in most organic solvents, mineral acids and caustic alkali solutions on heating; dissolves with difficulty in carbon tetrachloride; insoluble in ligroine and water.

Found %: C 65.67; H 6.46; N 12.82; S 14.73. $C_{12}H_{14}N_2S$. Calculated %: C 66.00; H 6.46; N 12.84; S 14.69.

The hydrochloride forms colorless prisms which gather in clusters (from alcohol), m.p. 148.5-149°, soluble in alcohol, acetone, and water.

Found %: Cl 13.97. $C_{12}H_{15}N_2SCl$. Calculated %: Cl 13.93.

VIII. 4(5)-Phenyl-2-n-butylmercaptoimidazole. This was prepared analogously to (V) from 2.07 g of 4(5)-phenyl-2-mercaptoimidazole and 2.38 g of normal butyl iodide in an alkaline solution prepared from 0.27 g of metallic sodium, 15 ml of alcohol, and 5 ml of water. The solution was heated at the boil 3 hours 40 minutes. The yield of oily substance, which was converted into the hydrochloride with m.p. 172-173°, was 2.7 g (99%).

The hydrochloride of 4(5)-phenyl-2-n-butylmercaptoimidazole forms colorless needles (from alcohol), m.p. 180-181° (decomp.); soluble in alcohols, acetone, and water.

Found %: C 58.19; H 6.52; N 10.55; S 11.73; Cl 13.31. $C_{13}H_{17}N_2SCl$. Calculated %: C 58.06; H 6.37; N 10.43; S 11.93; Cl 13.20.

4(5)-Phenyl-2-n-butylmercaptoimidazole, isolated from the hydrochloride, is a colorless thick oily substance, soluble in most organic solvents, mineral acid solutions and caustic alkalies on heating, insoluble in water.

IX. 4(5)-Phenyl-2-isoamylmercaptoimidazole. To a solution prepared from 1.21 g of metallic sodium and 70 ml of alcohol, 9.32 g of 4(5)-phenyl-2-mercaptoimidazole was added. When this dissolved, 8.05 g of isoamyl bromide was added and the solution boiled 1 hour. The solvent was removed under vacuum, water was added to the residue, and the oily substance which separated was extracted with ether. An alcohol solution of hydrogen chloride was added to the ether solution dried over sodium sulfate, and the resultant white precipitate was filtered off, washed with ether, and dried. The yield was 13.2 g (90%) of substance with m.p. 168-169°. The hydrochloride of 4(5)-phenyl-2-isoamylmercaptoimidazole forms colorless leaflets from alcohol, m.p. 170-170.5°, soluble in acetone, water and alcohol.

Found %: Cl 12.63. $C_{14}H_{19}N_2SCl$. Calculated %: Cl 12.54.

The base, 4(5)-phenyl-2-isoamylmercaptoimidazole, was obtained from the hydrochloride by dissolving it in alcohol and adding aqueous sodium carbonate solution; it forms small colorless needles (from alcohol), m.p. 81-83°, soluble in most organic solvents, mineral acids and caustic alkali solutions on heating, insoluble in water.

Found %: C 68.34; H 7.24; N 11.56; S 13.33. $C_{14}H_{18}N_2S$. Calculated %: C 68.23; H 7.36; N 11.37; S 13.02.

X. 4(5)-Phenyl-2-n-hexylmercaptoimidazole. This was prepared analogously to (IX) by the alkylation of 6.2 g of 4(5)-phenyl-2-mercaptoimidazole by normal hexyl iodide (7.5 g) in a solution prepared from 0.81 g of metallic sodium and 60 ml of alcohol. The solution was boiled 2 hours. The yield of substance with m. p. 136-136.5° was 9.6 g (91.8%). The hydrochloride of 4(5)-phenyl-2-n-hexylmercaptoimidazole forms colorless needles from alcohol, m.p. 138°, soluble in alcohol, acetone, chloroform, glacial acetic acid, and hot water, soluble with difficulty in cold water.

Found %: C 60.35; H 7.36; N 9.39; S 10.60; Cl 11.97. $C_{15}H_{21}N_2SCl$. Calculated %: C 60.66; H 7.13; N 9.44; S 10.80; Cl 11.95.

The base, 4(5)-phenyl-2-n-hexylmercaptoimidazole, is a colorless thick oily substance, soluble in most organic solvents, insoluble in water.

XI. 4(5)-Phenyl-2-p-nitrophenylmercaptoimidazole. To a solution prepared from 1.48 g of metallic sodium and 525 ml of alcohol, 11.1 g of 4(5)-phenyl-2-mercaptoimidazole was added. When this dissolved, 15.7 g of p-nitroiodobenzene was added, and the mixture boiled 4 hours. The solution remained alkaline to litmus. The solvent was then removed under vacuum, and the crystalline residue washed with water and dried. The yield was 18.0 g of substance with m.p. 122-130° (decomp.). To prepare pure 4(5)-phenyl-2-p-nitrophenylmercaptoimidazole, the substance was converted into the hydrochloride, which was recrystallized from alcohol. From the hydrochloride, 4(5)-phenyl-2-p-nitrophenylmercaptoimidazole was obtained and recrystallized for analysis first from acetone and then from alcohol; it forms yellow leaflets, m.p. 150-152° (with decomposition in a sealed capillary), soluble in most organic solvents, soluble with difficulty in ether and hydrochloric acid, insoluble in water, ligroine, carbon tetrachloride, and cold solutions of alkalies. The reaction with p-nitrochlorobenzene produced 4(5)-phenyl-2-p-nitrophenylmercaptoimidazole in the same yield.

Found %: C 60.15; H 4.03; N 13.80; S 10.62. $C_{15}H_{11}O_2N_3S$. Calculated %: C 60.58; H 3.72; N 14.13; S 10.79.

The hydrochloride forms pale yellow needles from alcohol, m.p. 242-243.5° (in sealed capillary); soluble in alcohol, acetone, and glacial acetic acid, soluble with difficulty in water.

Found %: Cl 10.75. $C_{15}H_{12}O_2N_3SCl$. Calculated %: Cl 10.63.

XII. 4(5)-p-Nitrophenyl-2-isoamylmercaptoimidazole. This was prepared analogously to (X) from 5.5 g of 4(5)-p-nitrophenyl-2-mercaptoimidazole and 3.75 g of isoamyl bromide in a solution prepared from 0.57 g of metallic sodium and 180 ml of alcohol. The yield of hydrochloride with m.p. 184-185° was 6.2 g (76.2%). The hydrochloride of 4(5)-p-nitrophenyl-2-isoamylmercaptoimidazole forms yellow crystals from alcohol, m.p. 185-186° (decomp.); soluble in alcohols, acetone, and water.

Found %: C 51.16; H 5.33; N 13.08; S 9.76; Cl 10.76. $C_{14}H_{18}O_2N_3SCl$. Calculated %: C 51.27; H 5.54; N 12.84; S 9.78; Cl 10.82.

The base, 4(5)-p-nitrophenyl-2-isoamylmercaptoimidazole, is a brown thick oily substance, soluble in most organic solvents, insoluble in water.

XIII. 1-Ethyl-4-phenyl-2-ethylmercaptoimidazole. To a solution prepared from 1.6 g of metallic sodium and 70 ml of alcohol, 5.5 g of 4(5)-phenyl-2-mercaptoimidazole and 10.3 g of ethyl iodide was added. The solution was heated 3 hours at 70-72°, and then the same time at the boil. The solution remained alkaline. The solution was evaporated to dryness under vacuum, water was added to the residue, and the oily substance was extracted with ether (85 ml). The ether solution was dried over magnesium sulfate and evaporated to dryness under vacuum. After vacuum drying at 50-60°, 6.1 g of pale brown oil was obtained, which was distilled under vacuum. The following fractions were obtained: 1st, 0.33 g, b.p. 130-150° (0.4 mm), m.p. of picrate 181-183°; 2nd, 4.85 g, b.p. 150-180° (0.4 mm), m.p. of picrate 183-184°; 3rd, 2 drops, b.p. 181-182° (0.4 mm), m.p. of picrate 170-172°. A mixed sample of picrates of the 1st and 2nd fractions melted at 182-184°, and of the 2nd and 3rd, at 176-179°. After recrystallization from alcohol all the picrates had m.p. 184-185°. A second distillation of the 2nd fraction gave 3.95 g of substance with b.p. 157-160° (0.55 mm); m.p. of picrate 184-185°. 1-Ethyl-4-phenyl-2-ethylmercaptoimidazole is a thick colorless liquid, soluble in most organic solvents and mineral acids, insoluble in water and solutions of alkalies. The picrate forms yellow prisms from alcohol, m.p. 184-185°.

Found %: C 49.41; H 4.36; N 14.77; S 6.91. $C_{15}H_{13}O_7N_5S$. Calculated %: C 49.43; H 4.15; N 15.18; S 6.95.

SUMMARY

1. 4(5)-p-nitrophenyl- and 4(5)-p-aminophenyl-2-mercaptoimidazoles have been prepared.

2. A number of sulfides, derivatives of 4(5)-phenyl and 4(5)-p-nitrophenyl-2-mercaptoimidazoles, have been prepared.

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